COMMERCIAL ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, MODES OF ASSAYING, AND PROXIMATE ANALYTICAL EXAMINATION OF THE VARIOUS ORGANIC CHEMICALS AND PRODUCTS EMPLOYED IN THE ARTS, MANUFACTURES, MEDICINE, &c.

WITH CONCISE METHODS FOR

THE DETECTION AND DETERMINATION OF THEIR IMPURITIES, ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

BY

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Third Edition, Rewritten and Revised

VOLUME II—PART III

ACID DERIVATIVES OF PHENOLS, AROMATIC ACIDS, RESINS, AND ESSENTIAL OILS

REVISED BY THE AUTHOR AND

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PREFACE TO VOLUME II, PART III.

With the issue of the present Volume, this treatise is again available in a completed form. The Chapter on AROMATIC ACIDS, which has been much enlarged and finds first place in this volume, originally preceded the section on TANNINS in the second edition of Volume III, Part I. In consequence of the enormous amount of successful research carried out in recent years on the chemistry of the RESINS and the ESSENTIAL OILS, the subject-matter of these chapters is almost entirely new, and occupies a space respectively five and ten times that of the same sections in the previous edition.

The compilation of this Volume was commenced as long ago as 1898 by its Author, but owing to his ill-health the work made only slow progress. Mr. Allen's untimely death at a comparatively early age was deeply regretted by all chemists, and especially by workers in the domain of Applied Chemistry. His recognised great ability and his untiring energy secured for this treatise a unique position among the standard works on chemical analysis. Those who were privileged to have known him felt not only the loss of a friend but of a master mind, whilst they now miss the benefit of his enlightening knowledge and great practical experience, which were ever at the service of any who solicited his help.

After his lamented death in 1904, I undertook the completion of the volume—a task carried out in ready obedience to a special and last request of the Author, who realised that he himself could not see the final completion of his work. I am personally responsible for the articles on the ANALYSIS OF CAOUTCHOUC, GUTTAPERCHA AND SUBSTITUTES (pages 289 to 326); and on the INDIVIDUAL ESSENTIAL OILS and the TERPENELESS OILS (pages 387 to 475, and 498 to 501). The article on TURPENTINE OIL (pages 475 to 498) was written by the Author and has been brought up-to-date by a few additions. A portion of the Author's manuscript was unfortunately lost, and as I was prevented by other duties from supplying the missing material, this section (covering pages 32 to 64) was prepared by Dr. Henry Leffmann of Philadelphia, the revision of this portion of the volume being left entirely in his hands.

The Author was much indebted to Mr. E. J. Parry for the collection of valuable material from which much of the manuscript for the Chapters on Aromatic Acids, Resins and Essential Oils (to page 385) has been prepared, and to Mr. L. Archbutt for supplying information for, and revising the manuscript of, the article on Turpentine Oil. I wish to express my personal thanks to Messrs. Parry and Archbutt for kindly revising certain of the proof-sheets, acknowledgment of which is duly made in the body of the work. Finally, I desire to record my indebtedness to Mr. John Evans for his aid in reading the proof-sheets, and for valuable assistance on botanical and pharmaceutical questions.

ARNOLD R. TANKARD.

County Analyst's Laboratory,
69, Dock Street,
Newport, Mon.
February 27, 1907.

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NOTE.

All temperatures are *Centigrade* unless otherwise specified.

The term "optical rotation" in this volume represents the observed angular rotation at 15° C. for 100 millimetres of the liquid, the sign $[\alpha]_D$ denoting the specific rotation of the substance.

In the absence of any statement to the contrary, all specific gravities refer to a temperature of 15.5° C., compared with water as unity at the same temperature.

ERRATA AND ADDENDA.

ADDITIONAL ERRATA IN PREVIOUS VOLUMES.

VOLUME I.

Page 53, line 19, *for* "Groves" *read* "Graves," and *for* "xlii, 120" *read* "xliii, 119."

Page 160, in table, *for* specific gravity of Scotch Whisky *read* 0.9416, and *insert the word* "proof" *before* "gallon."

Page 261, in formula, *for* "114" *read* "144."

Page 523, in Allen's scheme for analysis of cream of tartar, *for* "grain" in each case *read* "gramme." The *caustic alkali* referred to is *decinormal*. In paragraph "*b*," methyl-orange is to be used as indicator in the titration.

VOLUME II, PART I.

Page 140, line 24, *for* ".916" *read* ".926."

VOLUME II, PART II.

Page 165, line 18, *for* "0.1 cc." *read* "1.0 cc."

Page 277, line 20, *delete the words*, "but does not coagulate albumin."

VOLUME III, PART III.

Page 21, line 1, *for* "C_4" *read* "C_{24}."

VOLUME IV.

Page 57, footnote 1, line 6, *for* "Venturini" *read* "Venturoli."

Page 473, table in footnote 4, fourth line of figures, *for* "23.71" *read* "59.94."

ERRATA AND ADDENDA.

Page x, in Contents, line 3 from foot of page, *for* "Carvoxine" *read* "Carvoxime."
" 4, line 21, formula, the hydroxyl-groups are (1) and (2), and not (1) and (3) as given.
" 5, line 11 from foot of page, *for* "353" *read* "2."
" 8. The sodium phenolsulphonate described is the *para* salt.
" 8, line 27, *for* "36" *read* "30.6."
" 54, in heading of page, *for* "Tinctures" *read* "Tincture."
" 60, last line of page, *delete the words* "cinnamic acid."
" 61. Adulteration of liquid storax with cocoanut oil. See G. W. Morris, *Chem. & Druggist*, 1906, p. 902.
" 129, in heading of page, *for* "Acids" *read* "Acid."
" 150. Composition of commercial jalap. R. W. Moore, *J. S. C. I.*, 1906, p. 627.
" 154. The second columns of the table, in the case of each observer, refer to a second sample of the drug examined.
" 187. New acid in guaiacum resin. P. Richter, *Arch. der Pharm.*, ccxliv, 90.
" 211. Composition of commercial asafœtida. R. W. Moore, *J. S. C. I.*, 1906, p. 627.
" 215. E. D. Merrill supports Trimen and Bentley's statement that the source of the exported elemi is *Conarium luzonicum* (Gray) and not *C. commune* as generally given.
" 251, last line in end column, *for* "caraway" *read* "eucalyptus."
" 276, heading in table, *for* "Graviy" *read* "Gravity."
" 287. P. van Romburg has stated (1905) that guttapercha and pontianac contain lupcol acetate and cinnamate (Lupcol = $C_{24}H_{40}O$?).
" 287. Composition of balata. Tschirch and Schereschewski, *Arch. der Pharm.*, ccxliii, 358.
" 333, in heading of page, *for* "Alcohol" *read* "Alcohols."
" 343, *between the words* "the" *and* "process" *insert* "hydroxylamine."
" 357, 365. Constitution of diosphenol. See Semmler and McKenzie, *Berichte*, xxxix, 1906, p. 1158.
" 361. Determination of phenols in essential oils. Schryver's method (*Analyst* xxv, 18; xxx, 62) is merely applicable to those oils containing only phenols and terpenes (*e. g.*, oils of cloves and pimento).
" 368. (Footnote 1.) A German patent (No. 134,553 of 1904) describes the production of artificial camphor by the action of alkali on bornyl hydrogen oxalate, produced as described in this footnote.
" 378. Wallach has recently proved the existence of two isomeric thujones, and in all probability a third isomer exists (*Annalen*, cccxxxvi, 247).
" 387. For a valuable monograph on the botanical origin of the Indian grass oils, see O. Stapf, *Kew Bulletin*, No. 8, 1906. Many of the oils hitherto *classed as Andropogon oils are now re-named as species of Cymbopogon.* Thus citronella oil is derived from *C. Nardus;* lemongrass oil from *C. flexuosus;* and palmarosa oil from *C. Martini.*
" 391. Citral is probably not the only aldehyde present in certain lemongrass oils, and thus the percentage of citral as determined by the absorption method, may be above the truth (Umney & Bennett; H. E. Burgess; E. J. Parry, *Chem. and Druggist*, 1907, p. 138; Feb. 2nd; Feb. 16th).
" 427. Ethyl citrate is being added to lavender oil. This adulterant represents more than double its weight of linalyl acetate (C. T. Bennett, *Chem. & Druggist*, 1906, Nov. 3rd).
" 446. Certain "weedy" peppermint oils of American origin at present on the market are much less soluble in 70 per cent. alcohol (*viz.* 1 in 6) than normal distillates.
" 455, line 28, *for* "the foregoing figures" *read* "the figures in the table (page 456)."
" 458. Rose oil distilled *in vacuo* has a high specific gravity and contains phenylethyl alcohol in large amount. Parry has recently examined samples of high specific gravity (.862 to .880 at 30°) and stated to be prepared by a special process, which were adulterated largely with geraniol, &c.
" 469, line 11, *for* "formula" *read* "formulæ."
" 508, optical rotation of cajuput oil is "To —3."

AROMATIC ACIDS.[1]

The true aromatic acids form a well-defined and important group of bodies containing a benzene-nucleus. Many of them occur ready-formed, either free or combined, in resins, balsams and essential oils, as well as in animal organisms; many are prepared synthetically from constituents of coal-tar. The most important series of aromatic acids bears the same relation to benzene and its homologues that the aliphatic acids bear to methane and its homologues (paraffins), and the two series of acids present many points of resemblance. Just as acetic acid may be regarded as the type of a fatty or aliphatic acid, so benzoic acid is representative of the aromatic or cyclic acids; while a parallel to acrylic acid may be found in cinnamic acid, to glycollic and lactic acids in salicylic acid, to succinic acid in phthalic acid, and so on. The following tabular arrangement renders these analogies more evident:—

Fatty (Aliphatic) Acids.		Aromatic (Cyclic) Acids.	
Formic,	$H.COOH$	Benzoic (phenyl-formic),	$C_6H_5.COOH$
Acetic,	$CH_3.COOH$	Toluic (phenyl-acetic),	$C_7H_7.COOH$
Propionic,	$C_2H_5.COOH$	Xylic (phenyl-propionic),	$C_8H_9.COOH$
Acrylic,	$C_2H_3.COOH$	Atropic (α-phenyl-acrylic) / Cinnamic (β-phenyl-acrylic)	$C_6H_5.C_2H_2.COOH$
Propiolic,	$C_2H.COOH$	Phenyl-propiolic,	$C_6H_5.C_2.COOH$
Glycollic,	$CH_2(OH).COOH$	Salicylic (hydroxybenzoic),	$C_6H_4(OH).COOH$
Glyoxylic,	$CH(OH)_2.COOH$	Protocatechuic (dihydroxybenzoic),	$C_6H_3(OH)_2.COOH$
Erythric,	$C_3H_4(OH)_3.COOH$	Gallic (trihydroxybenzoic),	$C_6H_2(OH)_3.COOH$
Succinic,	$C_2H_4:\begin{cases}COOH\\COOH\end{cases}$	Phthalic,	$C_6H_4:\begin{cases}COOH\\COOH\end{cases}$

[1] The Author is indebted to Mr. E. J. Parry for perusal and criticism of this Section.

All, or nearly all, the aromatic acids in the foregoing table may be extracted by ether from their aqueous solutions. When heated with lime, they split up into carbon dioxide and benzene, hydroxybenzene, or homologues or analogues thereof. Thus:—

Phthalic acid, ...	$C_8H_6O_4 = CO_2 + C_7H_6O_2$,	Benzoic acid.
Benzoic acid, ...	$C_7H_6O_2 = CO_2 + C_6H_6$,	Benzene.
Toluic acid, ...	$C_8H_8O_2 = CO_2 + C_7H_8$,	Toluene.
Cinnamic acid, ...	$C_9H_8O_2 = CO_2 + C_8H_8$,	Cinnamene.
Salicylic acid, ...	$C_7H_6O_3 = CO_2 + C_6H_6O$,	Phenol.
Cresotinic acid, ...	$C_8H_8O_3 = CO_2 + C_7H_8O$,	Cresol.
Protocatechuic acid, ...	$C_7H_6O_4 = CO_2 + C_6H_6O_2$,	Catechol.
Gallic acid, ...	$C_7H_6O_5 = CO_2 + C_6H_6O_3$,	Pyrogallol.

In connection with the true aromatic acids, all of which contain one or more carboxyl-groups, CO.OH, the phenolsulphonic acids and certain allied compounds may be conveniently considered.[1] *The chief aldehydes, salts and esters of the aromatic* acids are also described in this section, as also are related bodies such as saccharin and acetophenone. The various bodies are classified under the following groups:—

Sulphonated Phenols and their Allies.
Benzoic Acid and its Derivatives.
Cinnamic Acid and its Derivatives.
Salicylic Acid and its Allies.
Protocatechuic Acid and its Allies.
Gallic Acid and its Derivatives.
Phthalic Acids.

SULPHONATED PHENOLS AND THEIR ALLIES.

By reaction with concentrated sulphuric acid, phenol may be converted into compounds in which one or more of the hydrogen atoms of the benzene-nucleus are replaced by SO_3H groups. The *sulphonic acids* thus obtained usually form soluble barium salts, and hence may be separated from any sulphuric acid which has not entered into the reaction by treating the aqueous solution of the product with excess of barium carbonate and filtering.

The phenol-sulphonic acids may also be conveniently separated from the crude product by diluting this with water and saturating the liquid with common salt, when the sulphonic acids separate out as crystalline sodium salts, which may be purified by recrystallisation.

The homologues of phenol, the diatomic and triatomic phenols, and other analogous bodies, also form sulphonic acids by treatment with strong sulphuric acid, the resultant compounds all

[1] Except the sulphonic acids and quinolinic acid (which is a member of the heterocyclic group) all the acids described in this chapter are members of the true hexacarbocyclic series.

being split up with formation of the original phenoloid bodies when heated with concentrated hydrochloric acid to a temperature between 100° and 200°. This general reaction is valuable, as the various isomers and homologues may usually be separated with comparative facility by fractional crystallisation in the form of salts of their respective sulphonic acids, and the phenols then regenerated by treating these sulphonates with hydrochloric acid.

Phenol Sulphonic Acids.

When phenol is treated with concentrated sulphuric acid it dissolves readily, with considerable rise of temperature. The product is a mixture of *ortho*- and *para*-phenol-monosulphonic acids, $C_6H_4(OH).SO_3H$.[1] When the phenol and sulphuric acid are slowly mixed, and the liquid prevented from becoming hot, the *ortho*-acid is chiefly formed, but much phenol remains unattacked. By heating the mixture for some time to 100° C., the conversion of the phenol into a sulphonic acid is nearly perfect, even when but little more than the theoretical proportion of sulphuric acid has been employed, but the ortho-acid is in great part converted into *para*-phenolsulphonic acid (with some disulphonic acid), though some of the first body remains unchanged however long the heating at 100° be continued.[2] When the temperature is more elevated, the product, which in that case is nearly all *para*-acid, is frequently called sulphophenic acid or sulphocarbolic acid. (See page 6.)

By digesting phenol at 100° C. with a considerable excess of slightly fuming sulphuric acid, a ***phenol-disulphonic acid***, $C_6H_3(OH)^{(1)}(SO_3H)^{(2)}(SO_3H)^{(4)}$, is produced.[3] The solutions of this

[1] *Meta*-phenolsulphonic acid does not result from the direct sulphonation of phenol, but may be obtained by heating *m*-benzenedisulphonic acid with aqueous potassium hydroxide to 170°–180° (*Ber.*, 1876, 969). It has but little practical interest.

[2] Boiling with water is alone sufficient to convert the *ortho*-acid almost entirely into the *para*-acid.

[3] Phenol-disulphonic acid is employed by A. H. Gill for the determination of nitrates in water. From 10 to 25 c.c. of the sample is evaporated to dryness and the residue thoroughly mixed with 1 c.c. of a reagent prepared by heating 3 grammes of phenol and 37 grammes of concentrated sulphuric acid for six hours in a vessel immersed in boiling water. The product usually sets to a white crystalline mass on cooling, but this is easily melted when required. In the presence of nitrates, picric acid is formed with yellow colour. The mixture is taken up with 25 c.c. of water, ammonia added in excess, the liquid diluted to 50 c.c. and the colour compared with a standard, prepared for potassium nitrate, in the usual manner.

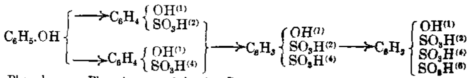
"Hermophenyl" is a mercuric sodium phenol disulphonate, and is used as an internal antiseptic. It is stated to have the constitution $C_6H_3(OHg)(SO_3Na)_2$.

acid and its salts are coloured deep red by ferric chloride. By heating phenol under pressure with sulphuric acid and phosphoric anhydride, a *phenol-trisulphonic acid*,[1] $C_6H_2(OH)(SO_3H)_3$, is produced, crystallising in short prisms and giving a blood-red colour with ferric chloride.[2]

The phenol-sulphonic acids may be separated from the excess of sulphuric acid by diluting the mixture with water and digesting the solution with excess of barium carbonate. From the liquid filtered from the insoluble barium sulphate the free sulphonic acid may be prepared by precipitating the barium by an equivalent amount of dilute sulphuric acid, or the potassium or sodium salt may be obtained by precipitating the solution with a carbonate of the alkali-metal. This process affords a useful means of separating the isomeric acids from each other. On allowing the solution of the potassium salts to crystallise, the salt of the *para*-acid separates first in hexagonal plates; while the *ortho*-salt, $C_6H_4(OH)SO_3K+2H_2O$, crystallises later in prisms which effloresce on exposure to the air (*Annalen*, ccv. 64).

When potassium ortho-phenolsulphonate is heated to 250° with caustic potash it yields catechol, or *ortho*-dihydroxybenzene, $C_6H_4(OH)^{(1)}(OH)^{(3)}$. The salt of the meta-acid when similarly treated yields *meta*-dihydroxybenzene or resorcinol, $C_6H_4(OH)^{(1)}(OH)^{(3)}$. The salt of the para-acid does not yield the corresponding para-dihydroxybenzene (quinol) under similar treatment, probably owing to its ready conversion into the meta-acid, which subsequently gives resorcinol. But quinone, $C_6H_4O_2$, is produced in large quantity by treating the parasulphonate with sulphuric acid and manganese dioxide,

[1] The sulphonation of phenol proceeds with the replacement of the *ortho*- and *para*- hydrogen atoms, just as in the nitration process, the sulpho- groups entering the *meta*- position with reference to one another:—



Phenol. Phenol-monosulphonic acids. Phenol-disulphonic acid. Phenol-trisulphonic acid.

[2] Similar series of bodies, the cresol- and xylenol-sulphonic acids, are obtained by the action of strong sulphuric acid on cresol (*Jour. Chem. Soc.*, liv, 280, 281) and xylenols respectively. In the sulphonation of meta-cresol, whatever the conditions, only one *mono*-sulphonic acid is obtained. By employing a larger proportion of sulphuric acid a *di*-sulphonic acid is formed, and by heating the cresol to 180° with fuming sulphuric acid, a *tri*-sulphonic acid is produced. When ortho-cresol is heated with sulphuric acid to 100° only orthocresol-parasulphonic acid is formed, but at the ordinary temperature *o*-cresol-*m*-sulphonic acid is also produced. When the concentrated aqueous solution of the latter acid is heated, it is converted into the former acid (*Ber.*, xx, 3089, 3209).

while neither the meta- nor ortho-sulphonate yields quinone by oxidation.

The following table shows the characters of the three isomeric phenol-monosulphonic acids and some of their salts:—

	Ortho-Acid. $C_6H_4\begin{cases}OH^{(1)}\\SO_3H^{(2)}\end{cases}$	Meta-Acid. $C_6H_4\begin{cases}OH^{(1)}\\SO_3H^{(3)}\end{cases}$	Para-Acid. $C_6H_4\begin{cases}OH^{(1)}\\SO_3H^{(4)}\end{cases}$
Free acid, ...	At ordinary temperature, liquid; sp. gr. 1.400. Crystallises at 8° to 10°, and boils at 130°.	Crystallises in fine needles containing 2 aqua.	Syrupy liquid; or hydrated, highly deliquescent needles.
Potassium salt, .	Melts at 240°, resolidifying to a vitreous mass. Long flat prisms containing 2 aq. Very soluble.	Melts at 200° to 210°. Confused efflorescent microscopic needles or scales containing 1 aq.	Melts at 400°. Anhydrous elongated hexagonal tables. Moderately soluble.
Sodium salt, ...	Indistinct crystalline masses containing 1½ aq.	Flat needles or rhombic tables containing 1 aq.	Long prisms containing 2 aq.
Barium salt, ...	Indistinct crystalline masses containing 2 aq. Very soluble.	Small laminæ of microscopic needles containing ½ aq. Easily soluble.	Long silky matted needles containing 3 aq.
Lead salt, ...	Indistinct tables containing 1 aq. Very slightly soluble.	Large rhombic tables containing 3 aq.	Long bundles of needles containing 2 aq. Basic salt, nearly insoluble.
Cupric salt, ...	Pale blue prisms.	Thin bright green rhombic prisms containing 6 aq.	Deep blue plates, resembling cupric sulphate. Contains 10 aq.

The phenol-sulphonic acids are very stable bodies, and are not decomposed by boiling with caustic alkalies.

By heating the free phenol-sulphonic acids or their salts with hydrochloric or dilute sulphuric acid under pressure, they are all decomposed completely with more or less facility, phenol being reproduced:—$C_6H_4(OH)SO_3K+H_2O=C_6H_5.OH+KHSO_4$. (Compare page 353.)

ORTHOPHENOL-SULPHONIC ACID.[1] $C_6H_4OH^{(1)}SO_3H^{(2)}$

This body has been employed as an antiseptic under the names "*aseptol*," "*sozolic acid*," and "*sulphocarbol*." It is obtained, together with more or less of the para-acid, by mixing equivalent quantities of phenol and strong sulphuric acid in the cold, and removing unacted-on sulphuric acid by adding barium carbonate. The free sulphonic acid is then obtained by treating

[1] H. E. Armstrong and some other authorities prefer the name phenol-orthosulphonic acid to orthophenolsulphonic acid, on the ground that it is the sulphonic acid which is the ortho-modification, not the phenol.

the filtered liquid with an equivalent amount of sulphuric acid, and again filtering.

Orthophenolsulphonic acid is soluble in water in all proportions, and is also soluble in alcohol and glycerol. It has very little corrosive action, and is practically non-poisonous. It is stated to have an antiseptic action three times as powerful as that of phenol, while the sodium salt is still more energetic. In its general reactions ortho-phenolsulphonic acid resembles the para-acid, into which it is converted by heat.

With ferric chloride, orthophenolsulphonic acid gives an intense violet coloration, resembling that produced by salicylic acid; and when taken by animals in doses of 5 to 10 grains, the urine gives the same reaction in a marked manner. Exposed to the light, a solution of this acid becomes deeply coloured.

Aseptol is a 33 per cent. aqueous solution of orthophenolsulphonic acid. It should have a specific gravity of 1.155, leave no residue on ignition, and should give no precipitate with barium chloride.

PARAPHENOL-SULPHONIC ACID. SULPHOPHENIC ACID.

$$C_6H_4 \begin{cases} OH^{(1)} \\ SO_3H^{(4)} \end{cases}$$

This substance, also called *sulphocarbolic acid*, is produced commercially by the direct action of concentrated sulphuric acid on phenol. If the acids are diluted beyond a certain point no action takes place. Moderate heating and the presence of excess of sulphuric acid over the theoretical quantity are conditions facilitating the completeness of the reaction. Paraphenolsulphonic acid with some admixture of the ortho-acid results, the latter body being subsequently more or less eliminated by fractional crystallisation of the potassium salts.

Phenol is not miscible with sulphuric acid before combination, nor much more soluble in dilute sulphuric acid than in water, but it is miscible in all proportions with concentrated sulphophenic acid, and in less than half its bulk of sulphophenic acid diluted with four volumes of water. Addition of more water precipitates phenol, which is again dissolved on addition of sulphophenic acid. These facts are important, for they show that sulphophenic acid cannot be purified from phenol by addition of water. Phenol may, however, be removed by repeatedly agitating the solution with ether free from alcohol; or the acid may be neutralised by soda, and the resultant sulphophenate crystallised from alcohol.

Paraphenolsulphonic acid may be concentrated to the condition of a syrupy liquid, and has been obtained in colourless,

hydrated, extremely deliquescent needles. It is soluble in water and in alcohol, but insoluble in ether or chloroform.

Sulphophenic acid is a powerful antiseptic and its solutions coagulate albumin, but these properties are not shared by the sulphophenates until after addition of acetic acid. The free acid and its salts do not suffer decomposition in aqueous solution even when exposed to the air, and their solutions are not decomposed by boiling. The commercial *sulphocarbolates* are salts of paraphenolsulphonic acid.

Phenolsulphonic acid and its salts are decomposed into phenol and sulphuric acid when heated with concentrated hydrochloric or dilute sulphuric acid in sealed tubes to 140° C.

A characteristic and delicate test for sulphophenic acid is to boil the liquid for a minute or two with an equal bulk of strong nitric acid, and then to neutralise the solution with potassium hydroxide. A yellow colour, due to the formation of potassium picrate, will be produced in a liquid containing 1 part of phenolsulphonic acid in 50,000 of water. Phenol itself gives the same reaction. The reaction of sulphophenic acid with nitric acid also results in the formation of sulphuric acid. Hence, if any sulphates originally present be removed by the addition of excess of barium chloride, and the solution be then boiled with nitric acid, white insoluble barium sulphate will be thrown down if a sulphophenate were present, and from its weight the amount of sulphophenic acid may be calculated. ($C_6H_6SO_4$: $BaSO_4$ :: 174 : 233.) The yellow liquid contains picric acid.

Another delicate test for paraphenolsulphonates is the production of a deep purple colour with ferric chloride. The reaction is also produced by ortho- and meta-phenolsulphonates, salicylates, etc. The colour is discharged by acids.

By the action of excess of bromine on a solution of paraphenolsulphonic acid or one of its salts, tribromo-phenol is produced, and sulphuric acid or a sulphate formed. This reaction enables sulphophenic acid to be readily detected in presence of phenol, and its amount may be deduced from the weight of barium sulphate yielded on filtering off the precipitate and treating the acidified filtrate with barium chloride.

The *paraphenolsulphonates* are all soluble in water, and mostly soluble in alcohol, especially when hot, but are insoluble in ether. Several of them, notably the sodium and calcium salts, have been employed in medicine as a means of internally administering carbolic acid. Only distinctly crystalline specimens should be used, and they should have but a very faint odour of phenol.

The sulphophenates may be recognised by the tests for sulphophenic acid already described. The sulphophenates of the alkali-metals if ignited alone, or those of other metals if ignited

with sodium carbonate, leave a residue containing sulphate. This reaction, the formation of sulphate by treatment with bromine or boiling with nitric acid, and non-extraction by ether from acidulated solutions are characters which distinguish the sulphophenates from salicylates.

The presence of unconverted *phenol* in sulphophenates may be detected by acidulating the solution with dilute sulphuric acid and agitating the liquid with ether or chloroform. The phenol left on spontaneous evaporation of the ether may be detected by its odour and by the yellow colour developed on warming with nitric acid and then neutralising with caustic potash. A faint colour should be neglected, as it may be due to a trace of sulphophenic acid dissolved by the ether.

The barium, calcium, and lead salts of phenolsulphonic acid are more or less soluble. Hence sulphuric acid and *sulphates* may be readily detected and determined by addition of barium chloride to the original solution. *Barium* and *calcium* salts may be detected in phenolsulphonates by dilute sulphuric acid and ammonium oxalate respectively.

Sodium Phenolsulphonate, $NaSO_3.C_6H_4.OH$, is prepared by double decomposition from the barium salt, and is the sodium sulphocarbolate of the Pharmacopœias. It forms transparent rhombic crystals containing 2 aqua, which are readily soluble in water, and have a cooling, saline, slightly bitter taste. The salt is permanent in the air, but becomes anhydrous at 100°. At a higher temperature it evolves phenol and leaves a residue of sodium sulphate and sulphite amounting to 36 per cent. of the weight of the crystallised salt.

Aluminium Paraphenolsulphonate, $Al(C_6H_4SO_3.OH)_3$, may be prepared by double decomposition. It is very soluble in water, alcohol, and glycerol, and the solutions can be kept unchanged. The salt has been introduced under the name of "*Sozal*" as a material for antiseptic dressings.

Zinc Paraphenolsulphonate forms transparent efflorescent prisms or plates containing 1 aqua. It also occurs as a white powder. It should leave 14.58 per cent. of zinc oxide on strong ignition. The probable impurities are *sulphates*, *chlorides*, compounds of the *light metals*, and free *phenol*. If prepared by the B. P. process, a notable quantity of sulphate is certain to be present.[1]

[1] The British Pharmacopœia of 1885 directed the salt to be prepared "by heating a mixture of carbolic acid and sulphuric acid, saturating the product with oxide of zinc, evaporating and crystallising." The solution of the product was stated to be "only rendered faintly turbid" by barium chloride. The description in the B. Pharmacopœia of 1898 is even more discreditable, for while omitting the words "evaporating and crystallising," it describes the product as giving "only the slightest reactions with the tests for sulphates."

Other salts of phenolsulphonic acid are described on page 5.[1]

IODO-PARAPHENOLSULPHONIC ACIDS.

When one molecule of iodine (in the form of a mixture of potassium iodate and iodide) is added gradually to one molecule of potassium paraphenolsulphonate dissolved in excess of dilute hydrochloric acid, iodine at first separates, but is quickly reabsorbed, and after a short time the liquid sets to a dense mass of long thin prisms of *potassium diiodo-paraphenolsulphonate*, $C_6H_2I_2(OH).SO_3K+2H_2O$. This salt requires about 50 parts of water for solution, and when heated decomposes without melting at about 270°, with evolution of violet vapours of iodine. It yields with caustic potash an extremely soluble basic salt, $C_6H_2I_2(OK).SO_3K$. The *sodium salt* (normal) forms a white crystalline powder containing $2H_2O$, and is infusible at 200° C. It is odourless, has a faintly acid taste, is soluble in 13 parts of cold water and more readily in hot; and is also soluble in alcohol. The magnesium, aluminium, zinc, and lead salts are readily soluble in water and glycerol, but the silver and mercury salts are but slightly soluble. The *barium salt* is only slightly soluble in cold water, from which it crystallises in white glistening needles. The *zinc salt* forms long colourless needles, and the *copper salt* pale green monoclinic prisms.

Diiodo-paraphenolsulphonic acid is prepared commercially in the free state by treating di-iodobenzene with fuming sulphuric acid, saturating the diluted liquid with lead carbonate, filtering, and decomposing the soluble lead salt by sulphuretted hydrogen. On concentrating the filtered liquid, the acid is deposited in crystals which melt at 120° and decompose at 190° with liberation of iodine.[2]

Di-iodophenolsulphonic acid contains 42 per cent. of iodine, is odourless and is a useful substitute for iodoform. Both the free acid and its salts possess well-marked antiseptic properties and are employed in medicine under the name of "*Soziodol.*" "Easily soluble soziodol" is the sodium salt, and is commonly given in solution, while the potassium salt forms the "difficultly soluble"

[1] *Cosaprine* is the sodium salt of the sulphonic acid of acetanilide. It has the constitution $C_6H_4(NH.CO.CH_3)^{(1)}SO_3Na^{(4)}$, and may be regarded as sodium paraphenolsulphonate in which the hydroxyl-group has been replaced by an acetamido-group. It is an odourless, white, amorphous powder, of saline taste. It is a strong antipyretic, and presents the practical advantage of being readily soluble in water. Its solution should give no precipitate with barium chloride.

[2] In preparing the di-iodo-acid, a certain amount of mono-iodophenolsulphonic acid is produced. This body forms thick, colourless, rhombic crystals, and yields barium and calcium salts which are readily soluble in water.

modification (*Ph. J.* [3], xviii. 538, 621, 1006). The potassium and zinc salts are used in ointments. The mercury salt has been employed as a hypodermic injection in cases of syphilis.

PHENYLSULPHURIC ACID. PHENYL HYDROGEN SULPHATE.

$$C_6H_6SO_4; \ i.\ e.,\ (C_6H_5)HSO_4; \text{ or } SO_2\left\{\begin{array}{l}OH\\O.C_6H_5\end{array}\right.$$

This acid is isomeric with the phenol-monosulphonic acids, $C_6H_4(OH)HSO_3$. It occurs together with its homologue cresyl-sulphuric acid, $(C_7H_7)HSO_4$, as a potassium salt in the urine of the horse and other herbivora. These salts also occur in considerable quantity in human urine after taking carbolic acid, and traces are normally present. During exhibition of phenol the inorganic sulphates ordinarily present in urine are greatly reduced in amount or even wholly disappear, being converted into phenyl-sulphates. The quantity of sulphur existing in normal human urine in the form of phenolic and other ethereal sulphates averages one-tenth of that present as metallic sulphates. The ethereal sulphates are represented by the potassium salts of phenyl-sulphuric acid, indoxyl-sulphuric acid, skatoxyl-sulphuric acid [1] and similar compounds of catechol and quinol. E. Baumann has shown that if the inorganic sulphates be first precipitated by acidulating the urine with acetic acid and warming the diluted liquid witb excess of barium chloride, the filtered liquid will contain any cresyl-sulphates and phenyl-sulphates which may be present. On strongly acidulating the filtrate with hydrochloric acid and boiling it for one hour the phenolic sulphates will be decomposed, barium sulphate being precipitated together with resinous matter, from which impurity it may be freed by washing with hot alcohol.[2] On subsequently distilling the acidulated urine the distillate contains distinct traces of phenol, directly recognisable by the bromine-reaction (Vol. II, Part ii), and if the distillate be shaken with ether and the ethereal solution separated and cautiously evaporated, the residue gives a distinct blue coloration with ferric chloride (Vol. II, Part ii). On the contrary, from the original urine no phenol can be extracted by agitation with ether, a behaviour evidently due to the fact that the phenyl-

[1] These compounds are fully described in Vol. III, Part iii.

[2] If the filtrate be evaporated to dryness, and the residue fused with nitre, an additional quantity of sulphuric acid is formed, corresponding, in human urine, to 10–20 per cent. of the total sulphur excreted, but rising in anomalous cases to a larger proportion. The unoxidised sulphur exists in the urine partly in the form of cystin, a body having the composition $C_6H_{12}N_2S_2O_4$; but a portion is excreted in the form of thiocyanates.

sulphates are not decomposed till the urine is heated with acid.[1]

Baumann has actually isolated potassium phenyl-sulphate from horses' urine by the following process:—The liquid is evaporated at a low temperature, the residue extracted with alcohol, and the filtered liquid concentrated to a syrup and allowed to stand in a very cold place. The crystalline plates which form are filtered off, dried, and purified by recrystallisation from strong spirit. The pearly-white tables obtained consist of potassium phenyl-sulphate (*J. C. S.* (1876), xxix., 726).[2]

Potassium Phenyl-sulphate, $(C_6H_5)KSO_4$, may also be prepared by the action of potassium phenate on potassium pyrosulphate:—$(C_6H_5)OK + K_2S_2O_7 = K_2SO_4 + (C_6H_5)KSO_4$. It crystallises in transparent rhombic tablets which feel greasy to the touch. It is readily soluble in water and sparingly soluble in cold absolute alcohol, but dissolves somewhat more readily in boiling alcohol. The aqueous solution exhibits a fine blue fluorescence.

Potassium phenyl-sulphate decomposes on exposure to moist air, sometimes in a few minutes, into phenol and potassium hydrogen sulphate. A similar change occurs by boiling the aqueous solution for a few hours, or warming it for a few minutes with dilute hydrochloric acid, but it is not affected by acetic acid. On the other hand, potassium phenyl-sulphate is stable in presence of alkalies, and is only gradually attacked by caustic potash at 150° C. When the solid salt is heated to 150°–160° in absence of moisture it is converted into the isomeric potassium para-phenolsulphonate.

Phenyl-sulphates are readily distinguished from phenolsulphonates by the formation of phenol and a sulphate on heating the solution with hydrochloric acid. When solid potassium phenyl-sulphate is quickly heated to fusion, and then dissolved in water, the solution gives a ruby-red colour with ferric chloride.

[1] E. Davies has described a specimen of urine passed by a person recovering from poisoning by carbolic acid (*Pharm. Jour.*, [3], xiv. 473). It was almost black in colour, and on distillation with sulphuric acid gave a distillate containing both phenol and cresol. The phenol was recognised by the odour, the reaction with ammonia and sodium hypochlorite, and the formation of an abundant precipitate of tribromophenol (of characteristic crystalline form) and (tri) bromocresol on adding bromine. Only a trace of phenol distilled over when the addition of sulphuric acid was omitted, and no phenol could be extracted by ether.

[2] L. Brieger treats fresh urine with neutral acetate of lead in excess, filters, and treats the filtrate with basic lead acetate. The lead is removed from the filtered liquid by sulphuretted hydrogen, and the filtrate evaporated to a thick syrup and kept for some time in a vacuum. The potassium phenylsulphate forms plates which are recrystallised from hot absolute alcohol (*J. C. S.* (1884), xlvi., 1353).

Free phenyl-sulphuric acid is so unstable that its aqueous or alcoholic solution decomposes almost immediately. It has never been isolated.

Naphthol Sulphonic Acids.

The practical application of the various acids obtained by the sulphonation of α- and β-naphthol is chiefly confined to the production of colouring-matters. Hence their preparation and characters are described in Vol. III, Part i.

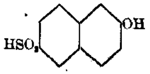
ASAPROL OR ABRASTOL appears to be calcium β-naphthol-β_3-monosulphonate, $[C_{10}H_6(OH)(SO_3)]_2Ca + 3\ H_2O$.[1] It forms an odourless, crystalline, bitter powder, neutral in reaction, and soluble in water and alcohol but not in ether. Asaprol is non-toxic and is recommended (in doses of 4 grammes) as an antithermic in typhoid fever and articular rheumatism. It is also used as a clarifier and antiseptic in wines. It gives a red coloration with mercuric nitrate, blue with ferric chloride, and purple with uranyl acetate. By these reactions asaprol may be readily detected in the urine after being taken internally. Mineral acids precipitate β-naphthol from asaprol, and if this precipitate be dissolved in sodium hydroxide, a blue colour is produced. With formaldehyde and sulphuric acid, asaprol gives a bright green fluorescence, which is destroyed on strongly diluting the liquid.

To detect asaprol or abrastol in red wine, A. S. Pintus shakes 10 c.c. of the cold sample with two grammes of animal charcoal, and adds to the filtered liquid an equal volume of a solution of mercuric nitrate containing nitrous acid (prepared by dissolving 10 grammes of mercury in 9.7 c.c. of nitric acid of 1.42 specific gravity and adding 3.5 c.c. of water to the solution). In the presence of abrastol, an immediate yellow coloration, with a golden fluorescence, is produced, the colour changing to rose on exposure to the air for a few minutes. In the case of white wines the preliminary treatment with animal charcoal is unnecessary, and the test in that case is capable of detecting 0.01 per cent. of the antiseptic. (See also Vol. II, Pt. ii, p. 206.)

Hydroxyquinoline Sulphonic Acids.

Several sulphonated compounds derived from quinoline have

[1] The acid has the constitution:—



been recently recommended as internal antiseptics. The following are the more important of these preparations:—

Diaphtol or Quinaseptol,	$C_9H_6N.SO_3H^{(2)}$
Diaphterine or Oxyquinaseptol,[1]	$C_9H_5N(OH)^{(1)}SO_3H^{(3)}$
Hydrargyraseptol,	$C_9H_5N(OH)SO_3Hg + 2NaCl$
Loretine,	$C_9H_4IN(OH)SO_3H$

The last of the above compounds is a meta-iodo-orthohydroxyquinoline sulphonic acid. It forms an odourless, yellow powder, insoluble in water and only slightly soluble in alcohol, ether, or oils. The sodium salt, known as "*soluble loretine*," dissolves in water with orange coloration. Both this compound and the free acid are powerful antiseptics used in surgery.

BENZOIC ACID AND ITS DERIVATIVES.

Benzoic acid is the central member of a group of highly interesting bodies, a considerable number of which possess more or less practical interest. They all contain the radical *benzoyl*, $C_7H_5O = C_6H_5.CO = Bz$, either intact or substituted.[2] In the following compounds the benzoyl-radical exists intact:—

Benzoic acid (Phenyl-formic acid),	$C_6H_5.CO.OH$
Benzoyl chloride (Benzoic chloride),	$C_6H_5.CO.Cl$
Benzoyl hydride (Benzoic aldehyde),	$C_6H_5.CO.H$
Benzoyl methide (Acetophenone),	$C_6H_5.CO.CH_3$
Benzoyl-glycocine (Hippuric acid),	$C_6H_5.CO.NH.CH_2.CO.OH$
Benzoyl-ecgonine,	$C_6H_5.CO.C_9H_{14}NO_3$
Benzoyl-methylecgonine (Cocaine),	$C_6H_5.CO.C_9H_{13}(CH_3)NO_3$
Benzoyl-acetyl-aconine (Aconitine),	$C_6H_5.CO.(C_2H_3O)C_{25}H_{39}NO_9$

In the following allies of benzoic acid substitution occurs in the benzoyl-radical itself:—

Methylbenzoic acids (Toluic acids),	$C_6H_4(CH_3).CO.OH$
Hydroxybenzoic acids (Salicylic acid, etc.),	$C_6H_4(OH).CO.OH$
Dihydroxybenzoic acids (Protocatechuic acid),	$C_6H_3(OH)_2.CO.OH$
Trihydroxybenzoic acids (Gallic acid, etc.),	$C_6H_2(OH)_3.CO.OH$
Carboxylbenzoic acids (Phthalic acids),	$C_6H_4CO.OH.CO.OH$
Nitrobenzoic acids,	$C_6H_4(NO_2).CO.OH$
Amidobenzoic acids,	$C_6H_4(NH_2).CO.OH$

[1] According to Crinon, diaphterine is merely a compound of sulphophenic acid with hydroxyquinoline.

[2] A colour-reaction for the detection of the benzoyl-group in organic compounds has been described by G. Denigès (*Analyst*, 1899, xxiv, 268). The indications are of very doubtful value.

Sulphobenzoic acids, ... $C_6H_4(SO_3H).CO.OH$
Sulphamidobenzoic acids,.............. $C_6H_4(SO_2NH_2).CO.OH$
Sulphamidobenzoic anhydride
(Saccharin), ... $C_6H_4\langle{}^{SO_2}_{CO}\rangle NH$

Many of these substituted benzoic acids have received important applications and are described in detail in the sequel.

Benzoic Acid. Benzene-carboxylic acid. Phenyl-formic acid. $C_7H_6O_2$; or, $C_6H_5.COOH$.

Benzoic acid occurs ready-formed in gum benzoïn, storax, and Tolu and Peruvian balsams, and in these and other resins also in the form of benzoic esters. It has also been found in the perfume known as *ylang-ylang*, in vanilla, in oil of jasmine, and in certain fruits, notably plums and cranberries.[1]

Benzoic acid is formed in numerous synthetic reactions, and is produced by the oxidation of a great number of organic bodies, including benzoic and cinnamic aldehydes, toluene, cumene, casein, gelatin, &c.

The following are the most important and interesting sources of benzoic acid:—

a. Gum Benzoïn.—The benzoic acid may be obtained by sublimation, or by exhaustion of the powdered substance with carbon disulphide. It may also be extracted from benzoïn by treatment with lime in the manner indicated on page 51.[2] Benzoic acid prepared from gum-benzoïn by sublimation is often more or less coloured, and has an aromatic odour.

b. Hippuric Acid (Vol. III, Part iii), contained in the urine of herbivorous animals, splits up into benzoic acid and glycocine on putrefaction of the urine, or when boiled with hydrochloric acid:—

$$C_6H_5.CO.NH.CH_2.COOH + H_2O = C_6H_5.COOH + CH_2(NH_2).COOH.$$

Benzoic acid prepared from this source is apt to retain a smell of urine which can be got rid of by careful sublimation.[3]

[1] *Benzoic acid* was discovered in the early part of the 17th century by the examination of the sublimate obtained on heating gum-benzoin. In 1775, Scheele showed how it could be purified, after extraction from the gum by lime-water. In 1832, the classical researches of Leibig and Wöhler were published, and not only was the nature of the *benzoyl* radical fully demonstrated, but the elementary composition of *benzoic acid* was established. The relation of benzoic acid to benzene was proved by Mitscherlich in 1834, by the distillation of the acid with lime, when benzene was obtained.

[2] The British Pharmacopœia (1898) makes no mention of benzoic acid prepared from gum-benzoïn by the lime process, though much of the purest commercial acid is obtained in this manner.

[3] In a case observed by the author the benzoic acid isolated from a mixture dispensed from a physician's prescription had a strong and offensive urinous odour.

c. Phthalic Acid, when heated with excess of slaked lime, yields a mixture of calcium carbonate and benzoate, from which benzoic acid may be readily prepared.

d. Trichlor-methylbenzene (benzenyl chloride), when heated with zinc chloride and glacial acetic acid, yields benzoic acid, acetyl chloride, and hydrochloric acid:—$C_7H_5Cl_3+2HC_2H_3O_2 = C_7H_6O_2+HCl+2C_2H_3OCl$. In order to avoid the evolution of hydrochloric acid, which carries off acetyl chloride with it, half the acetic acid may be advantageously replaced by zinc acetate. Or the formation of acetyl chloride may be avoided by heating benzenyl chloride with a little acetic acid and zinc acetate, and gradually adding the amount of water necessary for the formation of the benzoic acid.

e. Benzyl Chloride, C_7H_7Cl (1 part), is boiled with nitric acid (3 parts of 1.31 sp. gr.) and water (2 parts) in a flask with a reflux-condenser, until the odour of bitter-almonds disappears, and the liquid solidifies, on cooling, to a crystalline mass free from oily drops.

According to Guignet (*Compt. rend.*, 1891, p. 200), both gallic and tannic acids are readily converted into benzoic acid by reduction with zinc-dust and ammonia.

Benzoic acid crystallises from hot water in white lustrous scales or friable needles, but its crystalline habit is greatly modified by traces of impurity, so that the impure substance has been several times mistaken for an isomeric acid. When quite pure, benzoic acid is almost, if not quite, odourless,[1] but as met with in commerce it always has a well-marked odour, frequently smelling of benzoin, and sometimes of urine or almonds.

Benzoic acid has a specific gravity of 1.292, melts at 121°, and boils at 249°. It volatilises readily at a temperature much below its boiling-point, forming a beautiful feathery sublimate. The acid is somewhat volatile in a current of steam, and more or less with alcohol, benzene, and other volatile liquids.

Benzoic acid has a sharp taste, and produces a peculiar irritation in the throat. The vapour has a penetrating aromatic odour, attacks the eyes, and provokes coughing.

In cold water benzoic acid dissolves very sparingly, requiring 600 parts at 0° and 408 at 15° C.[2] In boiling water the solu-

[1] Four specimens of benzoic acid prepared by different methods and carefully purified were found by Perry to lose odour as the purification proceeded, becoming quite odourless when strictly pure. The merest trace of benzyl alcohol, benzyl benzoate, or benzaldehyde imparted a marked odour to the acid.

[2] The solubility of benzoic acid in water is much increased by the presence of certain salts, such as sodium phosphate.

SODIUM BENZENE-SULPHINATE is a compound obtained by dissolving

bility is 1 in 17. Benzoic acid is dissolved very readily by alcohol, ether, chloroform, amyl alcohol, benzene, petroleum spirit, carbon disulphide, and some fixed and volatile oils.

Pure benzoic acid is soluble in warm concentrated sulphuric acid without coloration, and is precipitated unchanged on dilution. By fuming sulphuric acid, or more readily by sulphuric anhydride, it is converted into a sulphonic acid. Ordinary nitric acid, even when boiling, does not affect it, but it yields a nitro-derivative with the fuming acid.

Benzoic acid is not acted on by chromic acid solution; but ozone in alkaline solution oxidises it to carbonic acid and water. When ingested by mammals, benzoic acid is converted into hippuric acid (Vol. III, Part iii), and appears in this form in the urine; but in the organism of birds it yields ornithuric acid, $C_{19}H_{20}N_2O_4$.

When distilled with excess of baryta or slaked lime, benzoic acid is decomposed into benzene and carbon dioxide, and when its vapour is passed over faintly-ignited zinc-dust it is reduced to benzoic aldehyde, C_7H_6O.

Benzoic acid is employed in medicine and in the manufacture of colouring-matters. It possesses decided antiseptic properties, being in this respect, according to some observers, superior to salicylic acid, and according to others inferior.

Analytical Reactions of Benzoic Acid and Benzoates.

Benzoic acid is distinctly acid to methyl-orange, but this indicator cannot be employed for its titration, as the end-reaction is very indefinite. Benzoic acid is sharply mono-basic towards phenolphthalein and Poirrier's blue, and may be accurately titrated by caustic alkali with the aid of either of these indicators.

Strong solutions of soluble benzoates are precipitated on addition of hydrochloric acid, owing to the slight solubility of benzoic acid in water. (Succinates give no precipitate with hydrochloric acid; but hippurates, cinnamates, and salicylates react like benzoates. Sulphuric acid should not be substituted for hydrochloric acid.) The separated benzoic acid dissolves on repeated agitation with ether, chloroform, or benzene. After washing the ethereal solution with water, the benzoic acid may be determined by adding alcohol and titrating with standard caustic alkali and phenolphthalein. If preferred, a solution of

benzoic acid in a concentrated solution of sodium sulphite. It is very soluble in water at the ordinary temperature, and the solution has been recommended as an antiseptic dressing for wounds. It is said to be more efficient than phenol, and to rank with mercuric salts and iodoform, without having the poisonous characters of the former or the disagreeable odour of the latter.

caustic soda or baryta may be added to the ethereal layer with constant agitation until the liquid is exactly neutral (to phenol-phthalein). The ethereal layer (which will retain any benzaldehyde or essential oils) is separated and the aqueous liquid evaporated to dryness, the residue dried at 100°, and the benzoate weighed.

Sodium amalgam, metallic magnesium, or aluminium gradually reduce a slightly acidified solution of a benzoate, with production of the characteristic odour of benzoic aldehyde.

Neutral ferric chloride precipitates neutral benzoates almost completely as a light red, bulky, basic ferric benzoate, insoluble in acetic acid. Succinates give with ferric chloride a reddish-brown, cinnamates a yellow, and hippurates a cream-coloured precipitate, meconates a deep red coloration, and salicylates a violet coloration. Benzoic acid is also distinguished from succinic and many other acids by not being precipitated by ammoniacal barium chloride in presence of alcohol. Magnesium benzoate is soluble in alcohol, but the succinate is insoluble.

Benzoic acid may be *separated* from fixed substances by sublimation, and may be determined in gum benzoin by that means.

Benzoic acid may also be approximately determined, in the absence of interfering substances, by converting it into a soluble neutral benzoate, and precipitating the cold solution with lead acetate, avoiding excess. The precipitate is filtered off, washed once with cold water, then with proof-spirit containing ½ per cent. of acetic acid, and finally dried at 100° and weighed. Its weight, multiplied by 0.5434, gives the amount of benzoic acid present.

Neutral benzoates are precipitated tolerably perfectly by cupric acetate or sulphate, especially in presence of alcohol, and the reaction may be employed for the determination of benzoic acid.

Rebière analyses metallic benzoates by carefully heating a known quantity with hydrochloric acid. The chlorine in the resultant chloride is determined by titration with silver nitrate. The method is not well-suited for the analysis of lithium benzoate, owing to the ready volatility of the chloride, and is evidently inapplicable to ammonium benzoate.

To determine the benzoic acid, the salt is treated with an amount of decinormal sulphuric acid exactly sufficient to combine with the metallic base, the quantity of which must be previously ascertained. The liberated benzoic acid is then titrated with standard caustic alkali and phenol-phthalein.

For the detection of benzoic acid in *foods*, E. Mohler (*Bull. Soc. Chin.* [3], **3**, 414) employs the reaction of hydrogen sulphide on an ammoniacal solution of symmetrical dinitro-

benzoic acid (1 : 3 : 5), whereby reduction takes place successively to amidonitrobenzoic and diamidobenzoic acid. In the case of beer, for example, 100 c.c. measure is rendered alkaline by sodium hydroxide and evaporated to a paste, which is acidified with hydrochloric acid, mixed with sand, and extracted with ether (20 c.c.). The ether is evaporated, and the residue moistened with sulphuric acid (2 c.c.), heated to 240° till acid vapours are evolved and charring takes place, when a few decigrammes of sodium nitrate are gradually added till the liquid becomes colorless. The clear liquid formed is poured into excess of aqueous ammonia and a drop of ammonium sulphide added. The least trace of benzoic acid is at once indicated by the production of a yellow coloration changing to reddish-brown.

F. M. Horn (*J. S. C. I.*, vii. 225) recommends the following method of determining benzoic acid in milk:—About 10 c.c. diluted with an equal volume of water is warmed with dilute hydrochloric acid (1 per cent.) until it coagulates. After filtering and washing the precipitate with warm water, the filtrate is evaporated and the residue taken up in 50 per cent. alcohol. A few drops of ammonia are added to this solution after filtration, the excess boiled off, and the liquid exactly neutralised and treated with its own volume of absolute alcohol. The benzoic acid is precipitated with copper sulphate and weighed on a tared filter as copper benzoate.

Commercial Benzoic Acid. The benzoic acid of commerce is liable to contain various impurities, some of which are due to its mode of preparation, while others are intentionally added as adulterants. Asbestos, boric acid, calcium carbonate and sulphate, sal-ammoniac and sugar are among the more or less apocryphal additions of the latter class.

Pure benzoic acid does not melt in boiling water, but some impurities impart this property to it, besides giving it greater solubility, and causing it to form smaller crystals of a different form from that usually assumed by the pure acid. On treating a sample of benzoic acid with ether, nearly all impurities and adulterants are left undissolved, except cinnamic acid, chlorobenzoic acid, and essential oil.

Inorganic impurities in benzoic acid can be detected and determined by subliming the sample, pure benzoic acid being readily and entirely volatile. If the residue chars on further heating, *sugar* or *hippuric acid* may be present. The former gives a smell resembling burnt bread, and the latter an odour of burnt feathers, and they may be readily distinguished in other ways. *Boric acid* is insoluble in ether, but dissolves in hot alcohol to form a solution which when kindled burns with a flame green at the edges. If this indication be obtained it should be

confirmed by repetition on the residue left on dissolving the sample in ether, as chlorobenzoic acid might also give rise to a green-edged flame.

Hippuric acid when present may be further detected by its incomplete solubility in ether; by its charring when heated with strong sulphuric acid; and by the evolution of ammonia which occurs when the sample is ignited with soda-lime. The last reaction may be employed quantitatively in the absence of ammoniacal salts. The proportion of hippuric acid may be approximately determined by agitating the sample with dilute hydrochloric acid and petroleum-ether or chloroform, when any hippuric (or succinic) acid remains undissolved. Samples of benzoic acid containing hippuric acid usually have a urinous odour, and redden or char when heated.

Salicylic acid may be detected by the production of a violet coloration with excess of ferric chloride. It may also be detected and determined by treating the warm aqueous solution of the sample with bromine-water, which throws down the salicylic acid completely as a white, voluminous precipitate, while benzoic acid gives no reaction. (Compare page 75.)

Cinnamic acid is said to be often present in considerable proportion in benzoic acid prepared from benzoin. It is best detected by its reaction with manganous salts (see page 40), and by the smell of bitter-almond oil produced on warming the sample with sulphuric acid and potassium bichromate. Cinnamic acid lowers the melting point of benzoic acid (page 41).

Chlorinated compounds are indicative of the presence of synthetic benzoic acid and should never be present in an acid prepared from natural sources. They may be detected by dissolving the sample in alcohol, moistening some asbestos with the solution, igniting it, and placing a beaker moistened with silver nitrate over the flame. If chlorinated products were present, a milky deposit of silver chloride will be produced. P. N. Raikow (*Chem. Central.*, 1899, 1, 1043) states that if a portion of the sample be heated on a platinum wire over a bunsen flame, and the evolved vapours allowed to come into contact with a few drops of an alcoholic solution of phloroglucol-vanillin contained in an inverted porcelain dish and held over the flame, a red colour will be developed in presence of organic chlorinated compounds.

Traces of *hydrochloric* and *sulphuric acids* are frequently present in commercial benzoic acid, owing to the method of preparation.

Sugar is recognised by its insolubility in ether, ready solubility in cold water, and by the blackening which occurs when the sample is heated with strong sulphuric acid. When present in quantity it may be detected by the taste of the sample, and

in *smaller quantity* by the taste of the residue left undissolved by ether or chloroform.

Ammonium chloride (*Sal-ammoniac*) is detected by shaking the sample with cold water, when a solution is obtained with which silver nitrate gives white curdy silver chloride insoluble in nitric acid. This proves the presence of a chloride only; the presumption that ammonium chloride is present is confirmed if the sample evolves ammonia on treatment *in the cold* with caustic alkali. In presence of ammonium chloride and other ammoniacal salts, the soda-lime test for hippuric acid is inapplicable, unless the sample be first shaken with cold, moderately concentrated hydrochloric acid, in which ammonium chloride dissolves, while hippuric acid is nearly insoluble.

Essential oil, which is very commonly present in benzoic acid made from gum benzoïn, causes the sample to turn brown when warmed with strong sulphuric acid. *Resinous* and *oily matters* will remain undissolved, together with any mineral matters, on treating the sample with sufficient warm dilute sodium hydroxide solution to neutralize the acid.

The *odour* of benzoic acid to some extent indicates its origin; but the acid from benzoïn is sometimes imitated by mixing the products from other sources with benzoïn, and subliming the mixture; or by adding vanillin to artificial benzoic acid. According to Hager, this factitious product may be detected by a mixture of solutions of ferric chloride and potassium ferricyanide. With the natural acid from benzoïn, the colour of this reagent is changed from yellow to blue in from 1 to 3 seconds; while with the product obtained by subliming the artificial acid over resin, from 20 seconds to 2 minutes are required.

The reduction of potassium permanganate has been proposed as a test for the origin of benzoic acid, but its indications have been proved to be fallacious. Ammonio-nitrate of silver has also been recommended, the test being used at a boiling heat.

O. Jacobsen recognises the acid from gum benzoïn by the presence of *catechol*, which he detects by converting the acid into a sodium salt, drying, and shaking with ether. The ether being separated and evaporated, the residue is dissolved and the catechol recognised by its reducing action on cold ammonio-nitrate of silver and by other reactions.

Jacobsen (*Jour. Chem. Soc.*, xlvi, 1168) has further investigated the nature of the substances accompanying benzoic acid prepared from gum benzoïn. On treating such acid with solution of sodium carbonate, an oil remains undissolved, smelling of vanillin and of phenol. This may be separated by distillation into three fractions. The first, boiling between 200° and 210°, consists of methyl benzoate and guaiacol, which can be separated

by cold dilute caustic soda. The second and smaller fraction (boiling between 235° and 245°) when shaken with water yields catechol, while acetyl-guaiacol remains undissolved. The third and largest fraction (boiling between 280° and 330° C.) contains benzyl benzoate, benzophenone, and benzoyl-guaiacol, with traces of vanillin and other bodies. On saponification with alcoholic potash, and agitation with water and ether, benzyl alcohol and benzophenone pass into the ethereal layer, while the alkaline solution contains benzoic acid and guaiacol. The two latter bodies may be separated by adding sodium bicarbonate till the liquid is alkaline to litmus, and then agitating with ether, which will dissolve the guaiacol only.

METALLIC BENZOATES.

The metallic benzoates are mostly crystallisable and soluble in water and alcohol, but insoluble in ether. Some of them, such as the sodium and barium salts, are withdrawn from their solutions by animal charcoal, and calcium benzoate is decomposed by it, so that free benzoic acid can be extracted by treating the charcoal with ether.

The general reactions and methods of analysing metallic benzoates have already been described (page 16).

Benzoic acid decomposes carbonates in aqueous solution, but when a current of carbon dioxide is passed through an alcoholic solution of potassium benzoate, potassium carbonate separates out.

Commercial benzoates are liable to contain much the same impurities as benzoic acid (page 14), especially *hippuric* and *chlorobenzoic acids*, *sulphates*, and *chlorides*. The two former impurities may be detected by acidulating the solution of the benzoate with hydrochloric acid and agitating with ether. Benzoic and chlorobenzoic acids pass into the ethereal layer, while hippuric acid remains (undissolved) in the aqueous liquid. The chlorobenzoic acid or other organic chlorine compounds may then be detected by allowing the bulk of the ether to evaporate spontaneously, adding alcohol, igniting, and testing the products of combustion for hydrochloric acid, as described above.

SODIUM BENZOATE, $NaC_7H_5O_2+H_2O$, crystallises in colourless needles. The salt is soluble in 1.7 parts of water at 15° if the acid used for its preparation were pure, but has a lower but varying solubility if chlorobenzoate or hippurate be present. Sodium benzoate receives an extensive application in America in the preservation of articles of food.

POTASSIUM BENZOATE, $2KC_7H_5O_2+H_2O$, forms concentrically grouped needles.

LITHIUM BENZOATE forms a crystalline powder or small shining

scales, soluble in 4 parts of cold or 25 of boiling water, and in 12 parts of cold or 10 of boiling alcohol. It is liable to contain much the same impurities as sodium benzoate (see above) and lithium citrate (Vol. I).

CALCIUM BENZOATE, $Ca(C_7H_5O_2)_2+3H_2O$, crystallises in granules or feathery needles, and is less soluble in hot water than in cold.

MANGANOUS BENZOATE is soluble in water (distinction from cinnamate).

FERRIC BENZOATE is obtained as a flesh-red precipitate by mixing solutions of neutral benzoates and ferric chloride. It is decomposed by washing with water into a soluble acid and insoluble basic salt.

CUPRIC BENZOATE, $Cu(C_7H_5O_2)_2+2H_2O$, crystallises from hot water in light blue needles or plates united in spherical masses. It is one of the least soluble of the benzoates.

LEAD BENZOATE is crystalline and difficultly soluble.

MERCURIC BENZOATE, $Hg(C_7H_5O_2)_2$, forms long silky crystals soluble in hot water, but very sparingly soluble in cold water. It is more readily dissolved by water containing chlorides or iodides. According to Rebière (*Pharm. Jour.*, 1887, i, 82), mercuric benzoate as met with in commerce is of very variable composition, as exemplified by the following analyses:—

	A.	B.	C.	D.	Theory.
Mercury,	54.78	52.80	42.60	45.12	45.25
$C_7H_5O_2$,	24.80	23.20	58.00	54.75	54.75
HCl,	16.79	traces	traces	——	——
HNO_3,	*traces*	*20.36*	*traces*	——	——

The salt can be obtained of almost theoretical composition (as was sample D) by precipitating mercuric chloride with excess of caustic soda, washing the mercuric oxide till free from chlorine, and boiling it with the calculated quantity of powdered benzoic acid in a little water, leaving the oxide in slight excess. On boiling the resulting powder with a large quantity of water it dissolves, and on cooling pure mercuric benzoate crystallises out.

BISMUTH BENZOATE. A basic salt, stated to have the composition $BiO.C_7H_5O_2$, is official in France. It is prepared by treating benzoic acid with freshly-prepared, moist bismuth hydroxide. The salt is amorphous and commercial samples show somewhat varying composition.

BENZOIC ESTERS.

The esters of benzoic acid are mostly highly aromatic liquids. They may be prepared by the action of benzoic chloride or anhydride on the alcohol, or by passing dry hydrochloric acid gas

through a solution of benzoic acid in the alcohol corresponding to the ester required. Several are of practical interest.

METHYL BENZOATE, $CH_3.C_7H_5O_2$, an aromatic liquid boiling at 199°, is used to a limited extent in the preparation of artificial fruit-essences and flavourings.

ETHYL BENZOATE, $C_2H_5.C_7H_5O_2$, may be prepared by dissolving three parts of benzoic acid in two of absolute alcohol and passing a stream of dry hydrochloric acid gas through the liquid. The product should be distilled, and the distillate shaken with water, separated from the aqueous liquid, dried over calcium chloride, and again distilled. Ethyl benzoate is a very fragrant liquid, boiling at 213°. It is employed in the production of artificial fruit-essences (see Vol. I), but is valueless in perfumery.

PROPYL BENZOATE boils at 229°, and *butyl benzoate* at 247° C.

BENZYL BENZOATE, $C_7H_5.C_7H_5O_2$, is a natural constituent of Peru and Tolu balsams (page 54). It forms compact lustrous crystals of aromatic odour, melts at 20° to 21°, and boils at 323° C. At its melting-point it has a specific gravity of 1.227.

The so-called "cinnameïn" of Peru balsam consists of a mixture of benzyl benzoate and cinnamate, in which the former constituent largely predominates. Benzyl benzoate is the constituent to which the efficacy of Peru balsam in the treatment of scabies is due. The synthetic ester has the advantage of being of constant composition and free from colour and odour, while it does not cause the irritation, due to the presence of free acid, which is sometimes a consequence of using Peru balsam. Benzyl benzoate has been introduced into commerce by the Berlin Aniline Company under the name of "*Peruscabin.*" A 25 per cent. solution of the ester in castor oil is known as "*Peruol.*"

EUGENYL BENZOATE, $C_{10}H_{10}O.C_7H_5O_2$, prepared by heating together eugenol and benzoyl chloride, forms the "*Benzeugenol*" of medicine. It has been employed as an antiseptic in cases of tuberculosis. It forms colourless, odourless, bitter crystals, very slightly soluble in water, but easily soluble in hot alcohol, ether, chloroform, and acetone. Benzeugenol melts at 70.5°, and gives a purple coloration with strong sulphuric acid. The formation of eugenyl benzoate is the basis of Thoms' method for the determination of eugenol in essential oils.

GUAIACYL BENZOATE, or BENZOYL-GUAIACOL, $C_6H_4(OCH_3).O.CO(C_6H_5)$, also called "*Benzosol,*" is recommended as a useful substitute for guaiacol in phthisis. It has the advantage over the latter of being tasteless and odourless. Benzosol forms small colourless crystals, melting at 50°. It is almost insoluble in water, but is readily soluble in hot alcohol, ether, and chloroform.

Benzoic Anhydride. Benzoyl Oxide. $O \left\{ \begin{array}{l} C_6H_5.CO \\ C_6H_5.CO \end{array} \right.$

This compound is the exact analogue of acetic anhydride. It may be prepared: (1) By heating benzoyl chloride with silver, or sodium, benzoate ($BzCl + AgOBz = Bz.O.Bz + AgCl$). (2) By digesting benzoyl chloride or benzotrichloride with anhydrous oxalic acid. (3) By the action of lead nitrate on benzoyl chloride (*Ber.*, xvii, 1881, p. 1282). (4) By the action of sulphuric acid containing 4.6 per cent. of water on benzotrichloride. (5) According to Minnuni (*Gazzetta*, xxii, ii, 213), when benzoyl chloride and pyridine are mixed an additive-compound is gradually formed, and this, when poured into water, is decomposed with formation of pure benzoic anhydride. A yield of 78 per cent. of the theoretical is said to be obtainable by careful manipulation.

Benzoic anhydride crystallises in rhombic prisms melting at 42° C. It boils at 360°, and dissolves readily in alcohol or ether. It is but little affected by cold water, but on boiling with water readily undergoes hydrolysis with formation of benzoic acid. By boiling with alcohol it yields *ethyl benzoate.* This and similar reactions render benzoic anhydride a valuable reagent for the production of benzoic esters, and it is employed for that purpose in the investigation of essential oils.

Benzoyl Chloride. Benzoic Chloride. $C_6H_5.COCl$

Benzoyl chloride may be prepared by the action of phosphoric chloride on benzoic acid, or by the action of chlorine on benzaldehyde. It is a liquid of penetrating odour. It boils at 198°, and solidifies at a low temperature, the solid melting at —1°. It is isomeric with the *chlorobenzaldehydes*, $C_6H_4Cl.COH$, and is a valuable reagent in organic synthesis.

Commercial benzoyl chloride is usually contaminated with chlorobenzoic chloride, and frequently with benzaldehyde and its chloro-derivatives. These impurities cause synthetic compounds prepared with it to contain chlorine compounds difficult to remove.

Benzoic Aldehyde. Benzaldehyde. C_7H_6O; *i.e.*, $C_6H_5.COH$

Benzoic aldehyde forms the major part of the essential oils of bitter almond, cherry-laurel, peach-kernels, and many other vegetable products, especially of members of the natural order *Rosaceæ.*

It is now extensively manufactured synthetically by several methods, including the following:—

(1) By the careful oxidation of benzyl alcohol, $C_6H_5.CH_2OH$.

(2) By the distillation of a mixture of calcium benzoate and formate.

(3) By the action of chromyl chloride, CrO_2Cl_2, on toluene.

(4) *By the action of lead or copper nitrate on benzyl chloride.* By this process the greater part of the commercial synthetic benzaldehyde is prepared. Two parts of benzyl chloride, $C_6H_5.CH_2Cl$ (prepared by the action of chlorine of hot toluene), are boiled with three parts of lead, or copper, nitrate and ten parts of water under a reflux-condenser for several hours. The operation should be conducted in an atmosphere of carbon dioxide. Half the liquid is then distilled off and the oil separated from the aqueous distillate. The product may be purified by conversion into its sulphite compound, but it will still contain traces of chlorine compounds.

(5) Benzaldehyde may also be prepared fairly economically by heating benzidene dichloride, $C_6H_5.CHCl_2$, under pressure with water and sodium hydroxide or milk of lime, or with glacial acetic acid and zinc chloride.

Pure benzaldehyde is a thin colourless liquid of high refractive power. It has a peculiar, very agreeable odour like that of bitter almond oil, and a burning aromatic taste. Its specific gravity is 1.0636 at 0° and 1.0504 at 15° C. It solidifies at —13.5° and boils at 179°. Benzaldehyde is soluble in about 300 parts of water, and is miscible in all proportions with alcohol and ether.[1]

On exposure to the air benzaldehyde absorbs oxygen greedily, and is converted into a crystalline mass of benzoic acid, $C_7H_6O_2$.[2] It is also oxidised by boiling with chromic acid mixture, or manganese dioxide and sulphuric acid; but is only slowly attacked by nitric acid, even when boiling.

When heated with solid caustic alkali, benzaldehyde evolves hydrogen and yields a benzoate. By treatment with water and sodium-amalgam, it is reduced to benzyl alcohol. Benzyl alcohol and a benzoate are also formed when benzaldehyde is treated with strong caustic alkalies.

Like all true aldehydes, benzaldehyde forms crystalline compounds with acid sulphites. The sodium compound has the formula $C_7H_6O.NaHSO_3$.[3] Benzaldehyde also responds to the other general reactions of aromatic aldehydes. It reduces ammoniacal silver solution with the production of the usual silver

[1] The solubility of benzaldehyde in water is often erroneously stated as 1 in 30, which is ten times the true amount.

[2] The oxidation is much retarded by the presence of hydrocyanic acid, which is therefore often added to the artificial oil of bitter almonds.

[3] This insoluble crystalline compound is converted, in the presence of an excess of sodium acid sulphite, into a soluble compound of the formula $C_7H_6NaSO_3$.

mirror, but differs from aldehydes of the aliphatic series in being permanent in presence of alkalies, and in not reducing Fehling's solution. Ammonium hydroxide converts benzaldehyde into white crystalline *hydrobenzamide*, $(C_6H_5.CH)_3N_2$, melting at 110°, which is resolved by acids into ammonia and benzaldehyde. This reaction also distinguishes the aromatic aldehydes from those of the fatty series.

Synthetic benzaldehyde is largely used, for flavouring and perfumery purposes, as a cheap substitute for the natural essential oil of almonds. Most of the synthetic benzaldehyde of commerce contains traces of chlorinated compounds, which are particularly objectionable, since they have an irritating odour, and cause soaps perfumed with the impure substance to deteriorate and darken on exposure to light. Benzaldehyde can, however, be obtained quite free from such impurities, and soap scented with it does not change colour on exposure. As a perfume, artificial benzaldehyde is inferior to the natural oil of almonds.

Benzaldehyde is employed largely for the production of various synthetic products, such as malachite-green, cinnamic aldehyde, etc.

Essential Oil of Bitter Almonds.

The essential oil of bitter almonds, *Amygdalus communis* var. *amara*, together with the oils of several other kernels, such as those of the apricot and peach, owe their characteristic odour and flavour to benzaldehyde. To all intents and purposes the oils from these three sources are identical, and most of the foreign bitter-almond oil is in reality peach-kernel oil. The oil does not exist in the free state in the kernels, but results from the decomposition of a glucoside, *amygdalin*, $C_{20}H_{27}NO_{11}$, which breaks down in the presence of water under the influence of the natural ferment *emulsin* or *synaptase* into a mixture of dextrose, benzaldehyde and hydrocyanic acid,[1] according to the following equation:—$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + HCN + 2C_6H_{12}O_6$.

[1] O. Linde (*Pharm. Jour.*, [3], xviii, 537) believes that the action of the emulsin or synaptase of the bitter almond on amygdalin is limited to the formation of glucose and benzaldehyde-cyanhydrin, which latter on subsequent distillation with water is partially split up into benzaldehyde and hydrocyanic acid, of which the latter is soluble in water. Hence the distilled oil consists chiefly of benzaldehyde with from 20 to 30 per cent. of benzaldehyde-cyanhydrin which has escaped decomposition. Fileti states that cherry-laurel oil contains the same body.

According to Tilden, cherry-laurel oil consists of benzaldehyde, less than 2 per cent. of hydrocyanic acid, a volatile oil (possibly benzyl alcohol), convertible into benzoic acid by oxidation, and minute quantities of an odorous resin (*Pharm. Jour.*, [3], v, 761).

This reaction is also brought about by the action of dilute hydrochloric acid.

Amygdalin is a crystalline body without the least odour of benzaldehyde, and if the ferment be destroyed by means of heat or warm alcohol (or, according to Flückiger, by intense cold) no essential oil of almonds is obtained. Thus powdered almonds do *not yield any oil when treated with boiling water.* The usual process adopted is the removal of the fixed oil by expression, when the press-cakes are ground up and soaked for a day with twice their weight of water to which a little salt is usually added. Some trouble is often experienced on account of the frothing produced during distillation, due to the presence of a large quantity of albuminous matter. This may be remedied by treatment with boiling water *after* the ferment has exerted its full action. Pure oil of bitter almonds contains much hydrocyanic acid (*vide infra*), but the acid-free oil is a regular commercial article, sold as "Oil of Almonds. S. A. P." (*sine acido prussico*).

Approximately from 1 to 2 per cent. of essential oil is obtained from the bitter-almond kernels, and this possesses a much finer and more delicate odour than synthetic benzaldehyde. Bitter-almond oil is a yellowish liquid (which can be obtained colourless by rectification) of specific gravity 1.045 to 1.070. The latter gravity is, however, somewhat rare, and normal oils seldom range outside the limits 1.045 and 1.060. Oil of bitter almonds is optically inactive, and neutral to ordinary indicators when fresh. On exposure to air, it rapidly absorbs oxygen and deposits crystals of benzoic acid, at the same time becoming acid in reaction.[1]

The main constituent of essential oil of bitter almonds is benzaldehyde, but a notable proportion of hydrocyanic acid (4 to 8 per cent.) is present, and appreciable quantities of phenyl-hydroxyacetonitrile (the nitrile of mandelic acid), $C_6H_5.CH(OH).CN$.[2] This last-named body, also known as benzaldehyde-cyanhydrin, is formed by a direct combination of benzaldehyde and hydrocyanic acid. A glucoside of it is formed in the hydrolysis of amygdalin by yeast, when only one

[1] Baeyer and Villiger (*Ber.*, 1900, p. 1569) have suggested that the oxidation of benzaldehyde takes place in the following manner:—One molecule of benzaldehyde combines with one molecule of oxygen to form benzoyl-hydrogen peroxide, $C_6H_5CO.O.OH$. This body then reacts with another molecule of aldehyde, thus:—$C_6H_5.CO.O.OH + C_6H_5.COH = 2C_6H_5.COOH$.

[2] Benzoïn, $C_6H_5.CH(OH).CO.C_6H_5$, is stated to be present in some specimens of bitter-almond oil. It is a solid camphor-like body melting at 134°, and occurs most largely in samples of oil of high density, in the preparation or purification of which a high temperature has been employed. It gives a purple colour with strong sulphuric acid.

molecule of dextrose is split off and mandelo-nitrilo-glucoside is left. Mandelo-nitrile has a specific gravity of 1.124, and is easily decomposable. Hence normal almond oils containing from 1.5 to 4 per cent. of hydrocyanic acid have a specific gravity usually falling between the limits of 1.052 and 1.058. Oils containing a larger quantity of hydrocyanic acid, even up to 11 per cent., have been known to reach the very abnormal specific gravity of 1.096.[1]

When oil of bitter almonds is fractionally distilled, hydrocyanic acid passes over first, and then tolerably pure benzoic aldehyde.

Oil of bitter almonds may be deprived of its hydrocyanic acid in several ways. Treatment with water, mercuric oxide, lime, and ferrous chloride has been recommended. Mackay treats the oil for forty-eight hours with lime and solution of potassium hydroxide.

Hydrocyanic acid may be detected in bitter-almond oil by agitating the sample with water, and applying tests to the latter. Ferric chloride and ferrous chloride or sulphate should be added, and then solution of sodium hydroxide. On acidulating the liquid with hydrochloric acid, a bluish-green coloration or prussian-blue precipitate will be formed if hydrocyanic acid was present. An aliquot part of the aqueous solution may be employed for quantitative determination by precipitation or titration with silver nitrate.

A preferable method is to dissolve 1 gramme of the oil in 5 c.c. of alcohol and dilute with water to 50 c.c. Excess of ammonio-silver nitrate is then added, and the mixture well agitated for a few minutes. The solution is then slightly acidulated with nitric acid, and the precipitated silver cyanide collected, washed, dried, and weighed, or ignited in the air and the resultant metallic silver weighed. Five parts (nearly) of silver cyanide or 4 of metallic silver correspond to one of hydrocyanic acid.

Bitter-almond oil is stated to give a crimson coloration with strong sulphuric acid, becoming brownish on exposure to the air. If the crimson liquid be poured into water the red colour disappears, and a yellow precipitate is produced, which sometimes takes the form of globules.

Essential oil of peach-kernels is frequently sold as oil of bitter almonds, but the most common falsification is synthetic benzaldehyde. Occasionally alcohol is added, but this is not

[1] Schimmel & Co. (*Report*, April, 1893) added a 20 per cent. solution of hydrocyanic acid to a sample of bitter-almond oil which had a specific gravity of 1.054. In two days the specific gravity had risen to 1.074. It is thus clear that bitter-almond oils of high gravity contain comparatively large proportions of mandelo-nitrile.

always done with a fraudulent intention, as it is believed to retard oxidation. Sometimes the highly objectionable adulterant nitrobenzene (oil of mirbane) has been found.

Synthetic benzaldehyde, as already stated, usually contains marked traces of organic chlorine compounds. Some commercial specimens are free from these impurities and command a far higher price. The occurrence of organic chlorine compounds in oil of bitter almonds may be regarded as very strong evidence of adulteration with synthetic benzaldehyde. These chlorine compounds may be detected by passing the vapour of the sample together with hydrogen through a red-hot tube, as described under "Chloroform" in Vol. I; or the alcoholic solution of the sample may be inflamed, and a beaker moistened with silver nitrate solution held over the flame, when white silver chloride will be deposited.

Alcohol reduces the density of bitter-almond oil. It may be approximately determined by shaking the sample in a graduated tube with water or glycerin and noting the reduction in volume of the oily layer.

Nitrobenzene, $C_6H_5NO_2$, is, as mentioned above, sometimes used as an adulterant of bitter-almond oil, and has even been sold as a substitute under the name of "artificial essence of bitter almonds." Nitrobenzene has a density of 1.186, and hence is heavier than bitter-almond oil, from which it also differs in not yielding benzoic acid when a current of air is passed through it. It is an insidious poison, and should be rigidly excluded from articles of food.

The following method may be employed for the detection and approximate determination of nitrobenzene in bitter-almond oil. Some clean sand or emery is introduced into a wide-mouthed flask, and a known weight (about 10 grammes) of the sample to be tested added. This is followed by 40 c.c. of a saturated aqueous solution of acid sodium sulphite, the whole agitated briskly for a few minutes, and then shaken with ether free from alcohol. The benzaldehyde forms a compound with the sulphite, while any nitrobenzene dissolves in the ether. The upper layer is withdrawn by a pipette, more ether added, and the agitation repeated. The ether is again withdrawn by means of the pipette, the united ethereal liquids evaporated at a gentle heat, and the residual nitrobenzene weighed. The method is only roughly approximate. If the quantity of nitrobenzene be small, or there be any doubt as to its identity, four or five drops of the sample should be dissolved in alcohol, and heated for some time with hydrochloric acid and granulated zinc. The nascent hydrogen reduces the nitrobenzene to aniline, C_6H_7N. The liquid is filtered through wet paper, rendered alkaline with

solution of sodium hydroxide,[1] agitated with ether, and the ethereal layer removed and shaken with water and a few drops of dilute hydrochloric acid. The ether is separated, and a dilute solution of bleaching-powder is cautiously added to the aqueous liquid, when if nitrobenzene were originally present, a violet colour (mauve) will be developed. The process requires to be skilfully conducted. Reduction to aniline may be conveniently used for distinguishing bitter-almond oil from nitrobenzene, but not for detecting the latter in presence of the former. When this is required, the sulphite and ether process must be previously used for their separation.[2]

The following method for detecting and approximately determining nitrobenzene in bitter-almond oil is due to Maisch. Dissolve 1 c.c. of the sample in 12 c.c. of absolute alcohol, and add 0.75 gramme of fused caustic potash. Boil the liquid till it is reduced to about 4 c.c., and leave it to cool. If the sample be pure no crystals form, but a brown colour is slowly developed. The residual liquid is entirely soluble in water. In presence of nitrobenzene, brown crystals of azo-oxybenzene, $C_{12}H_{10}N_2O$, are formed, which are insoluble in water, and may be collected, dried by pressure, and weighed.

M. Boyveau states that an artificial oil of bitter almonds is occasionally met with having a density of 1.029 to 1.030. Its odour is more acrid than that of the natural oil, as may be observed by moistening strips of paper with the oil and exposing them to the air. To distinguish the natural from the artificial product, Boyveau shakes 1 c.c. of the oil with 1 c.c. concentrated sulphuric acid. The *natural oil* becomes currant-red, deepening in a few hours to a more intense and darker red, the mixture remaining perfectly clear. *Cherry-laurel* immediately takes a dark-red tint, without first passing through the delicate currant-red shade observed with bitter-almond oil. The mixture thickens somewhat, but remains perfectly fluid and clear. The oils from *peach- and apricot-kernels* behave somewhat similarly, but give an evanescent currant-red tint changing to a very dark red. *Artificial almond oil* first takes a red tint, and then immediately becomes brown, loses its transparency, and thickens, becoming a solid brownish mass in the course of twenty-four hours. By the loss of transparency and production of the brown colour, an admixture of 25 per cent. of the artificial oil in the natural oil of bitter almonds is said to be recognisable.

Essence of Bitter Almonds is the name given to a solution of

[1] When the nitrobenzene occurs in quantity, bleaching-powder may be added at once to the filtered liquid after nearly neutralising it with alkali.

[2] Most other essential oils can also be separated from benzaldehyde by means of acid sodium sulphite and ether.

commercial oil of bitter almonds in different proportions of rectified spirit. It is employed as a flavouring agent, for which purpose it should be quite free from hydrocyanic acid. *Almond flavour* is a solution of one part of the oil in seven of rectified spirit. The proportion of alcohol in these preparations is best determined by fractional distillation.

Bitter-Almond Water is a solution of bitter-almond oil in water. It is not a preparation of the British Pharmacopœia, but is official in several other countries. Its strength is uncertain. The proportion of hydrocyanic acid it contains may be determined with silver nitrate, after adding sufficient magnesium hydroxide to leave the sample slightly opalescent. The mixture should be left at rest for half an hour and then titrated with decinormal silver nitrate, using neutral potassium chromate as an indicator. Basic magnesium acetate is said to be preferable to magnesium hydroxide (Beckurts, *Jour. Soc. Chem. Ind.*, vi, 567; Linde, *Jour. Chem. Soc.*, lii, 1143). Bitter-almond water should retain its characteristic odour after the removal of all the hydrocyanic acid by the above process or by agitation with excess of silver nitrate.

To test for excess of hydrocyanic acid in bitter-almond water, 10 c.c. should be treated with 1 c.c. of decinormal silver nitrate and a few drops of nitric acid, and filtered. The filtrate should give no immediate precipitate on addition of more silver nitrate.

Cherry-Laurel Water (*Aqua lauro-cerasi, B. P.*), prepared by distilling fresh cherry-laurel leaves with water, and *Cherry Water*, from wild cherries, are preparations very similar to bitter-almond water; but the last-named becomes milky immediately on addition of ammonia, which is an effect not produced on laurel water till after the lapse of some time.

The Brit. Pharmacopœia requires cherry-laurel water to contain 0.10 per cent. of HCN, when assayed by titration with standard silver nitrate solution.

ACETOPHENONE. PHENYL-METHYLKETONE, $C_6H_5.CO.CH_3$.

This body results from the reaction of benzoyl chloride on zinc-methyl, or by distilling a mixture of calcium benzoate and acetate. It may also be readily prepared by the interaction of benzene and acetyl chloride in the presence of aluminium chloride. The two last-named methods are those usually adopted on the manufacturing scale.

Acetophenone crystallises in large laminæ, melting at 20° to a colourless, mobile liquid of about the density of water, boiling at 202° C. It has a very persistent odour, recalling that of bitter-almond and cherry-laurel water. It is nearly insoluble in water, soluble in 60 parts of glycerin and very soluble in alcohol,

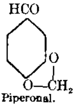
ether, chloroform, petroleum-spirit, and fatty oils. Dissolved in fixed oil of almonds, it is frequently administered in gelatin capsules.

Acetophenone is neutral and gives no coloration or characteristic reactiou with ferric chloride, hydrochloric acid, or sulphuric acid. By oxidation with chromic acid mixture it is converted into benzoic and carbonic acids. With nitric acid it gives a yellow coloration.

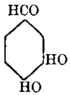
Acetophenone has hypnotic properties, and has been introduced into medicine under the name of "hypnone" (*Pharm. Jour.* [3], xvi, 445, 582).

Gallacetophenone. $CH_3.CO.C_6H_2(OH)_3$. This body, also known as *trioxyacetophenone*, and as "Alizarin Yellow C," may be regarded as a trihydroxy derivative of acetophenone, or as a methyl keto-compound of pyrogallic acid. It is a yellow powder, melting at 170° C., and is soluble in warm water, alcohol, ether, and glycerin. It is only very slightly soluble in cold water, but more so in solution of sodium acetate. It is used (in the form of an ointment) to a certain extent as a remedy for psoriasis, being a substitute for pyrogallol.

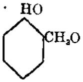
CONSPECTUS OF STRUCTURAL FORMULAS OF SOME SUBSTANCES DESCRIBED IN THIS VOLUME.



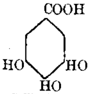
Piperonal.



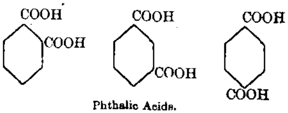
Protocatechuic Aldehyde.



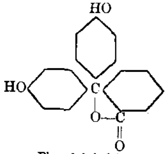
Guaicol.



Gallic Acid.



Phthalic Acids.



Phenolphthalein.

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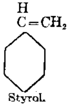
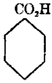
Phenol.

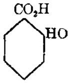
Benzaldehyde.



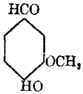
Styrol.



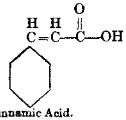
Benzoic Acid.



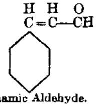
Salicylic Acid.



Vanillin.

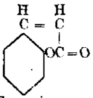


Cinnamic Acid.

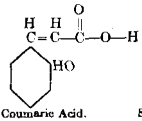


Cinnamic Aldehyde.

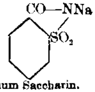
Saccharin.



Coumarin.



1-2 Coumaric Acid.



Sodium Saccharin.

Saccharin: $C_6H_4(CO)(NH)(SO_2)$. *1-2-sulphaminbenzoic anhydride; Benzoyl sulphinide; Benzosulphinidum* (U. S. Pharm., viii); *Glusidum* (Br. Pharm.).

Saccharin is an anhydride of 1–2 sulphaminbenzoic acid. It is prepared by several methods, one of which is as follows:—

Toluene is heated with concentrated sulphuric acid, the temperature not being allowed to rise above 100°. The product, which consists of a mixture of the three toluenesulphonic acids, is neutralised with lime, and the calcium sulphonates treated with sodium carbonate. The liquid is filtered, evaporated to dryness, and treated with phosphorous chloride in a stream of chlorine, by which the three toluenesulphonic chlorides, $C_6H_4(CH_3)SO_2Cl$, are formed. Of these the 1–2 and 1–4 forms predominate, the 1–3 form being present only in small proportion. The 1–2 form remains liquid; the others crystallize and the crystals are separated by means of a centrifuge. Upon the completeness of this separation depends largely the purity of the saccharin. The 1–2 toluenesulphonic chloride is treated with gaseous ammonia or with ammonium carbonate (or ammonium acid carbonate) by which the amid, $C_6H_4(CH_3)SO_2NH_2$, is formed, which, by oxidation by potassium permanganate, is converted into potassium derivative according to the following equation:

$$C_6H_4(CH_3)SO_2NH_2 + 2KMnO_4 = KHO + 2MnO_2 + 2H_2O + C_6H_4(CO)SO_2NK.$$

On the addition of a strong acid, the saccharin is precipitated. The crude material is often contaminated with by-products, among which is 1–4 sulphaminbenzoic acid. Numerous methods for the purification of the saccharin have been proposed, among which are the following:—

A. R. Ling (*Br. pat.*, *1893, 21417*) proposes treatment of the crude product with solution of sodium acetate. The saccharin passes into solution as a sodium compound; the 1–4 compound remains undissolved.

F. von Heyden (*J. S. C. I.*, 1893, 784), by crystallization of the solution containing the mixed salts (potassium, sodium calcium or magnesium) of the two forms, by which the 1–4 salt remains in solution, being much more soluble than the 1–2 form.

Saccharin is a white crystalline powder, with a faintly aromatic odor and intense, sweet taste; 1 part in 10,000 of water can be detected by the taste. It melts at 224°. The melting point is materially raised if the 1–4 compound is present. Its solubilities are: 1 part dissolves in 400 parts of cold water, 100 parts of boiling water, 25 parts of (90%) alcohol, and 120 parts of ether. It is also soluble in a mixture of ether and light petroleum. These immiscible solvents extract it from an (acidified)

solution in water. It is soluble in glycerol. Water containing alkali or alkali carbonates dissolves more than pure water. As already noted, the hydrogen atom of the imid-group may be replaced by other positives. Some of these derivatives are more soluble than saccharin itself and have more or less of its sweetness.

Sodium Saccharin, $C_6H_4(CO)(SO_2)NNa+2H_2O$, occurs in commerce under the name of "soluble saccharin" or "crystallose." It separates from hot water in readily soluble crystals. W. J. Pope (*Jour. Chem. Soc.*, 1895, 985) has observed that commercial saccharin yields a pure article in large crystals by a single crystallisation from acetone. The crystals show a momentary luminosity in the dark. Remsen and Burton state that when benzoyl sulphimide is boiled with dilute acids, it is first converted into 1–2-*sulphamidobenzoic acid*, $COOH.C_6H_4(SO_2NH_2)$, but on continued boiling it is completely changed into *hydrogen ammonium* 1–2-*sulphobenzoate*, $COOH.C_6H_4(SO_3NH_4)$. By evaporating a solution of saccharin with strong hydrochloric acid, orthosulphobenzoic acid and ammonium chloride are obtained.

The 1–4 sulphamido-benzoic acid, often present in considerable proportion in commercial saccharin, is unchanged by boiling with dilute acids.

When a solution of saccharin is evaporated with caustic alkali and the residue is heated to 250°, salicylic acid is formed, and may be detected by rendering the solution of the residue neutral or faintly acid, and adding ferric chloride, when the characteristic violet coloration will he produced. On igniting a mixture of saccharin and caustic or carbonated alkali, an odor of benzene is evolved, and on dissolving the residue in water acidulated with hydrochloric acid, the solution gives a white precipitate of barium sulphate on adding barium chloride. For quantitative purposes a little niter should be added during ignition. The saccharin represented may be found by multiplying the $BaSO_4$ by the factor 0.783.

Examination of Commercial Saccharin.

Apart from the by-products of manufacture, saccharin is liable to adulteration with diluents both organic and inorganic. Samples containing little else than inert mineral matter, such as calcium sulphate, have been found. As pure saccharin sublimes entirely at a temperature not much above its melting-point, ordinary mineral adulterants are indicated by notable amounts of ash.

The proportion of *saccharin* present in a sample may often be found by extracting the aqueous solution several times with ether, evaporating the ether and weighing the residue. Approximation

may be often obtained by titrating the aqueous solution with decinormal soda, using litmus or phenolphthaleïn. 1 c.c. of decinormal alkali neutralises 0.0183 gram of saccharin.

Sugars, *glucose* and *starch* will be left insoluble after repeatedly treating the solid sample with ether. A better separation from sugar can be obtained by repeatedly agitating the acidulated aqueous solntion of the sample with ether. If, after removing the ether, the aqueous layer be found, after neutralisation, to have a distinctly sweet taste, the presence of sugar is certain. The quantity can be ascertained by Fehling's solution after inverting the sugar, and preferably after removing the saccharin by ether. Saccharin does not reduce Fehling's solution.

Saccharin should not blacken when treated with cold concentrated sulphuric acid, and even on heating the mixture to 100° for ten minutes the coloration should merely be faint brown.

Benzoic or *salicylic acid* can be detected by heating a small amount of the sample with water, allowing the liquid to cool, filtering and testing the filtrate with ferric chloride. Benzoic acid will be shown by a turbidity; salicylic acid by a violet tint.

One of the usual by-products in commercial saccharin is 1–4 sulphamidobenzoic acid, $C_6H_4(COOH)SO_2NH_2$. For the detection of this, 1 gram of the sample should be shaken with 70 c.c. of ether at 15° for a few minutes, the ether drawn off as far as possible, the undissolved portion dried and its melting-point determined. This should not be above 224°. The amido-acid is much less soluble in ether than saccharin, hence the removal of the latter increases the *proportionate amount* of the impurity in the undissolved portion and thus raises the melting-point. The amido-acid melts at about 282°.

Determination of Saccharin in Commercial Samples.

The following process was devised by Hefelmann (*Pharm. Central Halle*, **36** (1895), 228): 10 grams of the sample are heated with 100 c.c. of 73 per cent sulphuric acid for five hours, the vessel being immersed in boiling water and frequently shaken. The mixture is then cautiously diluted with 100 c.c. of water, cooled, a crystal of pure 1–4 sulphamidobenzoic acid added, and the solution allowed to stand for at least twelve hours. When only small amounts of the 1–4 compound are present it may be necessary to allow the solution to stand for several days. The 1–4 acid separates almost entirely. It is collected in a Gooch crucible provided with a double strainer and an asbestos filter, washed with water until the acid reaction is removed, dried at 100° to constant weight and weighed. The loss due to the slight solubility of the precipitate in cold water is not serious. The material should melt at from 270°–280°.

The filtrate and washings are made up to 500 c.c. with water, 50 c.c. of this mixed with excess of magnesium oxide, and distilled. Ammonium hydroxide is formed, which is absorbed by dilute standard acid as in the Kjeldahl method. From the amount of ammonium nitrogen thus indicated the saccharin in the original material can be calculated: 1 part of nitrogen is equivalent to 13 parts of saccharin.

The total organic nitrogen in a sample of saccharin can be obtained by applying directly the Kjeldahl method. Small amounts of ammonium compounds may be present in commercial saccharin, especially if it has been exposed to the air. This accidental impurity can be detected by the ordinary tests for ammonium compounds.

Remsen and Burton (*Amer. Chem. Jour.*, 1889, 403) propose the following method for assay of commercial saccharin:—2 grams of the sample are boiled under a reflux-condenser for an hour with 100 c.c. of diluted hydrochloric acid (1 part of 1:17 acid to 8 parts of water), the clear solution evaporated to about 15 c.c., and the crystals of the 1–4 acid separated, after several hours' standing, and washed with cold water, dried at 80°, and weighed. The solution and washings, which contain hydrogen ammonium 1–2 sulphobenzoate, resulting from the decomposition of the saccharin and any hydrogen potassium orthosulphobenzoate originally present in the sample, are evaporated to dryness and the residue weighed. The potassium is next determined by weighing as sulphate. The difference between the total weight of the residue, and the potassium hydrogen 1–2 sulphobenzoate found, gives the amount of the hydrogen ammonium salt of this acid, and consequently of the saccharin of the sample.

C. Proctor (*Jour. Chem Soc.*, 1905, 242) states that the total amount of saccharin isomers (*i. e.*, 1–2 and 1–4 forms, the 1–3 form being, as noted above, present in negligible amount) can be determined by adding a weighed portion of the sample to a solution of potassium iodate and titrating the iodine set free. In such a mixture the true saccharin, *i. e.*, the 1–2 compound alone, may then be determined by one of the methods above given. Proctor found that some of the brands of saccharin now on the market contain as much as 99.5 per cent. of true saccharin, the remainder being moisture and mineral matter, organic impurities being inappreciable.

Detection of Saccharin in Foods and Beverages.

Saccharin, being an antizymotic, fulfils two requirements in foods and beverages,—a preservative and a substitute for sugar.

Many processes have been proposed for its detection; those given here are selected as being the most satisfactory.

General method. A suitable amount of the sample (50 to 100 c.c.) is slightly acidified with dilute sulphuric acid, and shaken with a mixture of equal parts of ether and light petroleum; a grade of light petroleum boiling below 60° is preferable. The solvent is evaporated at a gentle heat. The saccharin is left as a very sweet residue. It may be further identified by adding to the residue a few c.c. of a strong solution of sodium hydroxide, evaporating to dryness and heating to 210°–215° for thirty minutes. The saccharin is converted into salicylic acid, which may be detected by acidulating with sulphuric acid and testing with ferric chloride. Of course, the absence of salicylic acid must be ascertained before applying this method. If salicylic acid is present the residue from the ether-petroleum solution should be mixed with some dilute hydrochloric acid, bromine water added in excess, the liquid shaken well and filtered. Salicylic acid is completely removed as a bromine derivative. The filtrate is made strongly alkaline with sodium hydroxide, evaporated and heated as described.

Allen's method. This is especially adapted to the detection of saccharin in malt liquors, in which the ethereal extract contains bitter principles that interfere with the detection by taste. 0.030 gram of saccharin in 250 c.c. of beer can be readily detected. The liquid to be tested is concentrated to small bulk, acidulated with phosphoric acid, extracted with ether, the residue from the ether rendered alkaline with sodium hydroxide, ashed, and the ash tested for sulphate. If this is found, saccharin was present. Allen found that blank experiments gave no reaction for sulphate. The operation is facilitated if the sample is treated with a slight excess of lead acetate before extracting with ether. The slight amount of lead acetate remaining in the liquid does not interfere with the method. If it is desired to remove it, this will probably be done best by Sawyer's method, the cautious addition of strong solution of potassium oxalate. Care must be taken that the phosphoric acid is free from sulphuric acid.

The following test for saccharin has been described by J. H. Kastle (*U. S. Pub. Health and Mar. Hospital Serv.; Hyg. Lab. Bull.*, **26**, 31; also, *J. C. S.*, July, 1905, **2**, 503). A small quantity of the suspected solid (*i. e.*, the residue from an extraction) is mixed with a small amount of a mixture of 5 c.c. phenol and 3 c.c. of sulphuric acid, and heated for five minutes at 160°–170°. The mass is dissolved in cold water, and a little sodium hydroxide added; a purple red or rose red—according to the amount of saccharin present—will be produced. An excess of the phenol reagent should be avoided. 0.00025 gram of saccharin can be

detected, but with such minute amounts a very small quantity of the phenol reagent should be used, and the temperature should not go over 160°.

Salicylic and benzoic acids form only faintly yellow solutions. Coumarin does not give any reaction (page 49).

Special Method for Saccharin in Wine.

A substance occasionally occurring normally in wine may simulate the reaction for saccharin in the above test. To eliminate this source of error, Chace (*J. Amer. Chem. Soc.*, 1904, 1627) devised the following method:

The sample is extracted with ether alone and the extracting liquid evaporated. The residue is dissolved in water and extracted with light petroleum. This is evaporated, a small portion of the residue is tested for salicylic acid, then, and whether the latter is or is not found, the remainder of the residue is returned to the liquid from which it was extracted. The mixture is made up to 10 c.c., 1 c.c. of dilute sulphuric acid (1:3) added and then an excess of a dilute (about 5 per cent.) solution of potassium permanganate and the liquid brought to boiling. If salicylic acid was shown by the preliminary test, the boiling should continue for one minute, but if it is not present, the duration may be less. While the solution is still hot, a small piece of sodium hydroxide (enough to render the liquid alkaline) should be cautiously added. After a few moments the precipitated hydroxides are filtered off, the liquid evaporated to dryness, preferably in a nickel or silver dish, and heated to 210°–215° for twenty minutes. The residue is dissolved in water, acidified with dilute sulphuric acid, extracted in the usual way with ether, and tested for salicylic acid. If a reaction for this occurs, saccharin was present in the sample.

CINNAMIC ACID AND ITS DERIVATIVES.

Cinnamic Acid. Phenyl-acrylic Acid.

$$C_9H_8O_2 = C_9H_8O.OH = C_6H_5.CH:CH.COOH.$$

Cinnamic acid occurs free and as esters in liquid storax, Tolu and Peruvian balsams, in Sumatra benzoin, and in old oils of cinnamon and cassia, which sometimes deposit it in large crystals.

It may be prepared synthetically by several reactions, among which are the following:—

a. By the oxidation of cinnamic aldehyde, which constitutes the greater part of the oils of cinnamon and cassia.

b. By the saponification of styracin (cinnamyl cinnamate) or of cinnamein (benzyl cinnamate).

c. By heating benzaldehyde with acetic anhydride and sodium acetate.

d. By the action of sodium acetate on benzal chloride. This reaction is utilised for the preparation on the large scale:—

$$C_6H_5.CHCl_2 + NaC_2H_3O_2 = 2NaCl + C_6H_5.CH:CH.COOH + HC_2H_3O_2.$$

Cinnamic acid crystallises in colourless, monoclinic prisms or laminæ having a specific gravity of 1.247. It melts at 133° C. and distils with more or less decomposition at about 300°. If slowly distilled alone, or more readily if heated with lime, it splits into carbon dioxide and cinnamene, C_8H_8, a small quantity of stilbene, $C_{14}H_{12}$, being also produced.

Cinnamic acid dissolves sparingly in cold water (1 in 3500 at 17°), but readily in boiling water, alcohol, and ether.

In its general properties, cinnamic acid presents a close resemblance to benzoic acid, the following being the more ready points of distinction:—

	Cinnamic Acid.	Benzoic Acid.
Melting-point,	133·3°	123·3°
Boiling-point,	300°	249°
Reaction in neutral solution:		
With ferric salts,	Yellow.	Reddish.
With manganous salts,	White, becoming yellow and crystalline.	No precipitate.

Cinnamic acid is also distinguished from benzoic acid by the smell of bitter-almond oil developed on warming it with chromic acid mixture. The same odor is produced by boiling cinnamic acid with water and lead dioxide, the last body gradually becoming yellow, and being partially converted into lead benzoate.

When fused at a moderate temperature with caustic potash, *cinnamic acid is split up with evolution of hydrogen and formation* of potassium acetate and benzoate:—$C_9H_8O_2 + 2KHO = KC_2H_3O_2 + KC_7H_5O_2 + H_2$. The presence of an acetate in the product is a proof of the existence of cinnamic acid in the original substance.

Benzoic acid may be separated from cinnamic acid by crystallisation from boiling alcohol. The acids may also be separated by distillation in a current of steam, when benzoic acid nearly free from cinnamic acid passes over. By careful sublimation, the benzoic acid may also be completely separated, as little cinnamic acid volatilises below 200°.

Cinnamic acid may be detected in presence of benzoic acid by suspending the suspected compound in a 5 per cent. solution of uranium acetate and exposing it to direct sunlight. In a few

minutes the cinnamic acid is oxidised to benzaldehyde (recognised by its odour) and a brownish precipitate appears in the liquid (A. Jorissen, *Chem. Zeit.*, **25**, 1901, 11).

Cinnamic acid combines with two atoms of bromine when treated with excess of this reagent under suitable conditions. In this way cinnamic acid may be determined in admixture with benzoic acid, which does not take up bromine directly. The method of determination is the same as that described under "Salicylic Acid" (page 64).

J. Kachler (*Zeits. f. Chem.* [2], vi, 59) gives the following table showing the melting points of various mixtures of cinnamic and benzoic acids:—

Cinnamic Acid. Per Cent.	Benzoic Acid. Per Cent.	Melting-Point. °C.
100	0	133·3
99	1	131·8
90	10	126·6
80	20	118·0
70	30	108·2
60	40	98·7
50	50	84·3
40	60	87·1
30	70	101·4
20	80	106·4
10	90	111·5
1	99	118·2
0	100	123·3

According to T. Bokorny, while cinnamic acid (in the form of 0.1 per cent. solution) is a good bactericide, the sodium salt is much less active, a one per cent. solution being required to show any antiseptic action. The germicidal properties of cinnamic acid are stated to be greatly enhanced if used in conjunction with a little tartaric acid. The metallic *cinnamates* much resemble the benzoates. They are unimportant.

Cinnamene, styrolene, or phenyl-ethylene, $(C_6H_5)CH:CH_2$, exists in small quantity ready-formed in liquid storax (page 60), and may be extracted by distilling the balsam with water to which sodium carbonate has been added to neutralise the free cinnamic acid. The hydrocarbon passes over with steam, and collects as an oil on the surface of the distillate. Cinnamene may also be obtained synthetically, and, as stated above, by heating cinnamic acid alone, or in admixture with lime or baryta. The reaction in the latter case is exactly parallel to that by which benzene is produced from benzoic acid and methane from acetic acid.

Cinnamene is a colourless, mobile liquid, of specific gravity 0.925 at 0°, having a pleasant aromatic odor. It remains fluid at —10° C. and boils at 144°, the contents of the retort being liable to rise suddenly in temperature from formation of metacinnamene.

Cinnamene resembles ethylene in its property of combining readily with chlorine, bromine and iodine. The dibromide, $C_8H_8Br_2$, is most conveniently obtained by adding bromine to a solution of the hydrocarbon in chloroform. By oxidation, cinnamene is readily converted into benzoic acid.

Metacinnamene, (nC_8H_8) is formed slowly at the ordinary temperature, and readily on heating cinnamene in a sealed tube to 200°. It is a transparent, amorphous, odorless solid of high refracting power, softening on application of heat, when it may be drawn out into threads. On distillation, it is reconverted into cinnamene. Metacinnamene is insoluble in water and alcohol, and only very sparingly soluble in ether.

Stilbene, or diphenyl-ethylene $(C_6H_5)CH.CH(C_6H_5)$, crystallises in nacreous plates, melts at 124°, and boils at about 306°. It unites with bromine to form a dibromide, $C_{14}H_{12}Br_2$, crystallising in silky needles, which melts at 233°.

Cinnamic Esters.

METHYL CINNAMATE, $CH_3.C_9H_2O_2$, *forms crystals melting at* 33° and boiling at 263° C. It is an important constituent of the essential oil of the rhizomes of *Alpinia Malaccensis*, and is also present in the leaves of the same plant. Other oils derived from *plants of same species probably contain this ester.*

ETHYL CINNAMATE, $C_2H_5.C_9H_7O_2$, is produced by distilling together cinnamic acid, alcohol, and strong sulphuric acid; or by saturating a strong solution of cinnamic acid with hydrochloric acid gas. *It is a limpid liquid of 1.3 specific gravity, boiling* at 271° C. When treated with a mixture of strong nitric and sulphuric acids, avoiding rise of temperature, it is converted into a mixture of ethyl paranitrocinnamate and ethyl orthonitrocinnamate. The latter body crystallises in prisms which melt at 130°, the para-compound in fine, very thin, slightly yellowish needles which melt at 138.5° C. On heating the mixture of the two ethers with alcohol the ortho-compound only is dissolved, and is deposited on cooling in large yellowish needles. When treated with strong alkali, it is saponified with formation of ethyl alcohol and potassium orthonitrocinnamate, from which free orthonitrocinnamic acid, $C_9H_7(NO_2)O_2$, can be obtained by adding an acid. By treating this body with bromine it is converted into an additive compound of the formula $C_9H_7(NO_2)Br_2O_2$, which

by careful treatment with caustic soda yields sodium bromide and the sodium salt of orthonitro-phenylpropiolic acid, $C_9H_5NO_4$, or $C_6H_4(NO_2).C_2.COOH$. This body when acted on by a reducing agent, such as nascent hydrogen, glucose, or sodium xanthate, yields indigo-blue or indigotin, thus:—$C_9H_5NO_4 + H_2 = C_8H_5NO + CO_2 + H_2O$. These reactions offer a method for synthetic preparation of indigo-blue, but have been supplanted by the method in which naphthalene is used.

BENZYL CINNAMATE. Cinnamein. $C_7H_7.C_9H_7O_2$. This body exists ready-formed in Peru and Tolu balsams. It may be obtained with some admixture of cinnyl cinnamate by treating the former substance with carbon disulphide, separating the insoluble matter, and distilling off the solvent from the solution.

Benzyl cinnamate has an agreeable taste and feeble aromatic odour, resembling that of Peruvian balsam, but without the empyreumatic smell observable in the latter. It is commonly described as an oily liquid which is liable to solidify with conversion into a crystalline isomeric body called metacinnamein. But when obtained pure by boiling together benzyl chloride, alcohol, and dry sodium cinnamate, it forms short shining white prisms which melt at 39° C., and may remain liquid for a considerable time if cooled to 0°. Benzyl cinnamate has a density of 1.098 in the liquid state, and distils with slight decomposition between 225° and 235°. It is nearly insoluble in water, but is readily dissolved by alcohol, ether, carbon disulphide, etc.

By long exposure to air and light, benzyl cinnamate acquires an acid reaction. It is readily saponified by alcoholic potash, with formation of potassium cinnamate and benzyl alcohol, $C_7H_7.OH$.

PHENYL CINNAMATE, $C_6H_5C_9H_7O_2$. This melts at 72.5° and under a pressure of 15 mm. boils at 206°; at ordinary pressure it boils with decomposition. *Phenyl propyl cinnamate* occurs in small amount in Sumatra benzoin, in storax and yellow resin.

CINNAMYL CINNAMATE. Styracin. $C_9H_9.C_9H_7O_2$. This body occurs together with benzyl cinnamate in liquid storax, and Peru and Tolu balsams. It crystallises in tufts of beautiful prisms, which are devoid of smell or taste and melt at 44° to a liquid which remains viscous long after cooling. It distils without decomposition in steam heated to 180°. Cinnamyl cinnamate is insoluble in water and but sparingly soluble in cold alcohol or petroleum-ether, but is easily soluble in ether or carbon disulphide. When treated with alcoholic potash it is saponified with formation of potassium cinnamate and—

CINNAMYL ALCOHOL, Styryl Alcohol, or Styrone, $C_9H_9.OH$. When cinnamyl cinnamate is cautiously distilled with aqueous

potash, a milky distillate is obtained, and on saturating it with common salt the cinnamyl alcohol forms a creamy or oily layer on the surface. It may also be extracted from the distillate or the original liquid by agitation with ether.

Cinnamyl alcohol forms soft, silky needles having a sweet taste and an odour of hyacinths. It melts at 33°, and distils unchanged at 250° C. It is soluble in about 12 parts of cold water, a hot saturated solution becoming milky on cooling and remaining so for several hours, when the cinnamyl alcohol separates in crystalline needles, very soluble in alcohol and ether.

Cinnamyl alcohol possesses valuable antiseptic properties, being as powerful in this respect as thymol.

Cinnamyl alcohol is converted by cautious oxidation into cinnamic aldehyde and cinnamic acid. With chromic acid mixture it becomes hot and yields cinnamic acid, which separates on the surface, and on heating this becomes further oxidised to benzoic aldehyde.

Cinnamic Aldehyde. $C_9H_8O. = C_8H_7.COH.$

This occurs in oils of cassia and cinnamon, of which it constitutes the greater part. It may be produced artificially by the oxidation of cinnyl alcohol; by the dry distillation of a mixture of cinnamate and formate of calcium; and by saturating a mixture of benzaldehyde and acetaldehyde with hydrochloric acid, thus:—
$C_6H_5.COH + CH_3.COH = H_2O + C_6H_5.CH{:}CH.COH.$

Cinnamic aldehyde is a colorless oil, rather denser than water. It may be distilled in a vacuum, or with water free from air. On exposure to the air, it quickly becomes yellow and resinous, and acquires an acid reaction. It rapidly absorbs oxygen, especially in presence of moisture, and is converted into cinnamic acid. Chromic acid converts it into benzoic and acetic acids.

OIL OF CINNAMON. OIL OF CASSIA. The volatile oil of cinnamon is prepared by distilling the chips and refuse bark with water. Ceylon cinnamon yields from ½ to 1½ per cent.

The oil of Ceylon cinnamon is a pale yellow or reddish liquid, becoming red-brown and thicker on exposure to air, and finally separating crystals of cinnamic acid. It has a strong, but agreeable, cinnamon odor, and a sweet, pungent, aromatic taste. The specific gravity increases with the age of the oil. It remains clear at —10° C., but at a lower temperature (—20° C.) separates a stearoptene. It is readily soluble in alcohol, but not in cold petroleum spirit, and when fresh is neutral to litmus, becoming acid by oxidation.

The oil of Chinese cinnamon, commonly known as *oil of Cassia*, closely resembles the Ceylon product, except that its color is

deeper, its odor less delicate, its taste less sweet, and its specific gravity somewhat higher,—usually between 1.055 and 1.065. It is only slightly optically active, sometimes inactive. It should contain 70 per cent. cinnamic aldehyde, and even then may not be of high quality, as good samples contain 75 per cent. or even 80 per cent. In the London market the oil is graded by its aldehyde content, being sold as 70–75 per cent.; 75–80 per cent.; 80 to 85 per cent.

In addition to cinnamic aldehyde, cinnamon oil contains small amounts of eugenol and phellandrene. Some cinnamic acid may be present, the amount depending on the age of the sample, as the acid is produced by the oxidation of the aldehyde. The so-called "cassia stearoptene," described by Rochleder, is found only in old cassia oil. It is a complex aldehydic derivative. Cinnyl acetate is sometimes present

Hirschsohn (quoted from *Phar. Zeit. f. Russl.*, 30, p. 790, by Gildemeister and Hoffmann, "*Volatile Oils*," p. 386) found that owing to the solvent action of cinnamic acid on lead, the oils are apt to become contaminated with that element from the leaden vessels in which they are often imported. As the oils are used for food-flavors and sometimes in medicines for internal use the presence of lead is a danger.

Oil of Cinnamon Leaves. This is obtained by distilling the leaves of Ceylon cinnamon, but was at one time sold as oil of cinnamon root. Schimmel & Co. first pointed out the source. A product formerly sold as cinnamon-leaf oil has disappeared from commerce, and the true oil under its proper name has taken its place.

Oil of cinnamon leaves is a mobile, nearly colourless liquid, with odour recalling both cloves and cinnamon. The specific gravity ranges from 1.044 to 1.065. The oil has slight optical activity,—sometimes negative, sometimes positive. The chemical composition is not clearly made out, but it contains eugenol and only a small amount of cinnamic aldehyde.

Adulterations of Cinnamon and Cassia Oils. Oil of Ceylon cinnamon is liable to be adulterated with oil of cassia and oil of cinnamon leaves. The important data for detecting these are the amounts of eugenol and cinnamic aldehyde. Parry found many samples of cinnamon oil in the London market which had been adulterated with a mixture of cinnamon-leaf oil and synthetic cinnamic aldehyde added in large proportion to the genuine oil. He gives the following figures yielded by adulterated oils of this type:

Sp. Grav.	Per Cent. Cinn. Ald.	Per Cent. Eugenol.
1.036	25.5	45
1.042	24.8	47
1.051	27.0	49

A qualitative test for eugenol is often of use. A drop of genuine cinnamon oil dissolved in 5 drops of strong alcohol produces a pale green with ferric chloride, but leaf oil produces a deep blue.

The methods for detecting the prevailing adulterations of these oils have been especially studied in the laboratories of Schimmel & Co., whose publications are authoritative. Among these processes is determination of the "aldehyde content" upon which datum oil of cassia is now valued for commercial purposes. This is as follows:—

A special flask with a somewhat flat-bottomed bulb and long neck is used. The bulb holds about 100 c.c. The neck is about 13 cm. long, has a calibre of 8 mm., and is graduated to read to 0.1 c.c. The total capacity of the neck is a little over 6 c.c. The zero mark is slightly above the point at which the neck joins the bulb. 10 c.c. of oil are transferred to the flask and 10 c.c. of a 30 per cent. solution of sodium acid sulphite added. The mixture is shaken and immersed in boiling water. When the mass has melted, more sodium sulphite solution is added and, still shaking, the addition of small amounts of sulphite is continued until the volume of the mixture is about 75 c.c. The heating is continued until no more solid particles are present and the odor of cinnamic aldehyde has disappeared. When the clear oil floats upon the salt solution, the flask is removed from the bath, and when the contents are cold, sufficient sulphite solution is added to raise the lower limit of the oily layer to zero. The amount of oil is then read off, and by deducting this number from ten, the volume of cinnamic aldehyde in the sample is obtained. As the specific gravities of the aldehyde and other constituents are nearly the same, the reading may be taken as percentage by weight.

A good cassia oil will contain not less than 75 per cent. of cinnamic aldehyde. Only in rare instances does it rise above 90 per cent. Gildemeister and Hoffmann ("*Volatile Oils*," p. 389) state that genuine oils from China have been noted in which the aldehyde content was below 50 per cent., yet no adulteration could be recognised. The explanation of this could not be positively ascertained.

Oil of cinnamon should not contain less than 65 per cent. nor more than 75 per cent. of the aldehyde. When the amount of aldehyde is low, a determination of eugenol should be made. The most accurate method is that of Thoms, the eugenol being converted into benzoyl eugenol. Umney has suggested a simpler process,—namely, to determine the diminution of volume resulting upon shaking the sample with 5 per cent. solution of potassium hydroxide. The alkali dissolves some of the other constituents, but approximations can be made by the method. Adul-

teration may be assumed if the "eugenol content" is over 10 per cent.

J. Hanus (*Zeit. Unters. Nahr. u. Genussm.*, 1903, **6**, 617, 827; abst. *J. S. C. I.*, Oct. 30, 1903) found that cinnamic aldehyde, both pure and as it occurs in cinnamon and cassia oils, may be quantitatively precipitated in the form of semioxamazone,

$$C_6H_5.CH : CH.CH : N.NH.CO.CO.NH_2,$$

by treating an aqueous suspension with a solution of semioxymazide in hot water. 0.10 gm. of the aldehyde is weighed off, emulsified by agitation with 100 c.c. of water treated with 0.25 to 0.35 gms. of semioxamazide in 15 c.c. of hot water; the mixture is well shaken together, occasionally for three hours, then allowed to stand for twenty-four hours. The crystalline cinnamic-aldehyde semioxamazone is then collected on a tared Gooch filter, washed with cold water, dried at 105° C. for about four or five hours, then weighed. The weight of semioxamazone multiplied by the factor 0.6083 gives the amount of cinnamic aldehyde present. For the determination of the amount of aldehyde in cinnamon and cassia oils from 0.15 to 0.2 gm. should be employed.

To determine the amount of cinnamic aldehyde in cinnamon or cassia barks, from 5 to 8 gms. of the finely ground material are distilled with steam until about 400 c.c. of distillate has been collected. The volatile oil is extracted from the distillate by shaking out three or four times with ether, and after distilling off the ether, the oil is emulsified, and treated with semioxamazide as described above. By this method commercial cinnamic aldehyde has been found to yield from 99.21 to 100.66 per cent. commercial cinnamon oil from 46.78 to 80.51 per cent of cinnamic aldehyde; Ceylon cinnamon oil from another source, 79.05 to 80.33 per cent. Synthetic cassia oil, 95.19 to 95.58 per cent. of cinnamic aldehyde. Cinnamon bark was found to yield from 1.75 to 2.04 per cent. of aldehyde.

It is claimed that the method gives results more accurate than those of the bisulphite absorption process generally employed. With commercial cinnamic aldehyde, Allen obtained figures which were nearly 5 per cent. lower than those given by the bisulphite method. With the natural oils, however, the latter method gave results from 4 to 6 per cent. lower than this gravimetric process.

Adulterations of cassia oil, practised in former years with fatty oils, cedar-wood oil, and gurjun balsam, were easily detected, as the specific gravity was lowered by the adulterants and the free solubility in 80 per cent. alcohol was prevented. Cedar-wood oil and gurjun balsam have strong lævo-rotation.

Adulteration with a mixture of colophony and petroleum cannot be detected by these data. Schimmel & Co. (*Semi-annual Rep.*, Oct. 1889, 15; also "*The Volatile Oils*," Gildemeister and Hoffmann, 387) devised the following test for detecting this admixture:—

50 grams of cassia oil are weighed in a tared fractionation flask. A tube 1 meter long is attached as a condenser, and the oil is distilled with direct flame. At first, water passes off with crepitation, then the temperature rises rapidly to 240° and the bulk of the oil distils between 240° and 280°. When white fumes appear, indicating the beginning of decomposition of the residue, the distillation is stopped. The thermometer may rise to 280°–290° at this time. The flask is cooled and weighed. A good oil leaves a residue viscid and tough and not more than 10 per cent. of the original oil. The adulterated oil leaves a hard, brittle residue weighing more than 10 per cent. The oil forms a clear solution with 70 to 80 per cent alcohol. If petroleum is present, the mixture with such alcohol is turbid, and on standing some of the petroleum products separate.

Cassia oil that contains colophony and petroleum is soluble in 80 per cent. alcohol, but if only the latter is present the solution is turbid, the petroleum separating in oily drops. The following additional tests are taken from the work noted above:—

Gilbert (*Chem. Zeit.*, 13, 1406) suggests heating several grams of the sample in a watch-glass in a drying oven at 110°–120° to constant weight. He also states that the acid number is of value. An oil which upon distillation left 6 per cent. of residue had an acid number of 13. On adding 20 per cent. of colophony (having an acid number of 150) the acid number of the mixture was 40. An oil yielding 28 per cent. of residue had an acid number of 47.

Hirschsohn (*Pharm. Zeit. f. Russl.*, 29, 255) uses lead acetate as follows:—

1 c.c. of the sample is added to 3 c.c. of 70 per cent. alcohol, and this is mixed, drop by drop, with a freshly prepared solution of lead acetate in 70 per cent. alcohol until the volume of the latter solution is half that of the oil solution. A precipitate shows colophony. Hirschsohn states that as little as 5 per cent. can be thus detected.

COUMARIN, $C_9H_6O_2$.

This is sometimes called "tonka-bean camphor." It is the odoriferous ingredient of tonka, the seed of several species of *Dipteryx*, and also occurs abundantly in the leaves of *Liatris odoratissima*. It occurs also in the leaves of several other plants.

Coumarin forms colourless crystals having an odor recalling

that of vanillin but not so pleasant. It is very sparingly solubl in cold water, more so in cold alcohol (13 parts to 100 of alcoho at 16°); in hot alcohol it is freely soluble. It can be prepare synthetically by the interaction of sodium acetate, salicyli aldehyde, and acetic anhydride.

Kastle (see page 39) found that when the phenolsulphoni test for saccharin is applied to vanillin, the mixture become yellow and when the mass is heated to 160° for some minute it becomes red and finally black. The solution of the mass in wate becomes red on addition of sodium hydroxide. Coumarin give no color.

Coumarin is used in the preparation of perfumes, being mixe with other odoriferous principles, but its most important appli cation from a practical analytic point of view is as an adulteran and substitute for vanillin (see under "Vanillin").

Coumaric Acids. Hydroxycinnamic acids, $C_9H_8O_3C_6H_5(CH)$. $(CH)(COOH)(HO)$. Three isomeric forms are, of course known, respectively, 1–2, 1–3, and 1–4. The 1–2 forms occur i the leaves of species of *Melilotus* and in *Angræcum fragrans*. I can also be prepared by boiling coumarin with strong solution o potassium hydrate or sodium ethylate. It crystallises in colour less prisms which melt at 208° and are freely soluble in wate and alcohol. Solutions of alkali-metal coumarates show a brigh green fluorescence. By fusion with potassium hydroxide, 1– coumaric acid is converted into salicylic and acetic acids. B the action of nascent hydrogen it is converted into melilotic acid

1–4 coumaric acid occurs in small proportion in red acaroi resin, partly free and partly as a complex ester, and in larger pro portion in yellow acaroid resin. Esters of this acid are als found in Cape aloes and in the resin of *Picea vulgaris*. The aci can be obtained by hydrolysis of a glucoside *naringin*, whic occurs in the blossoms of *Citrus decumana* and may also b obtained by careful oxidation of 1–4 hydroxy-benzaldehyde.

Melilotic acid. 1–2 hydrocoumaric acid, $C_6H_4(HO)(CH_2)(CH_2)$ $(COOH)$, is obtained by the action of sodium amalgam on 1– coumaric acid or on coumarin. It occurs in association wit coumarin in yellow melilot (*Melilotus officinalis*). It melts a 81° and produces a bluish tint with ferric chloride. It yield salicylic acid when fused with potassium hydroxide. When dis tilled alone, it is converted into its lactone or anhydride, *hydr coumarin*, $C_6H_4\left\{\begin{matrix}CH_2\text{-}CH_2\\ O\text{—}CO\end{matrix}\right\}$ which melts at 25° and boils a 272° C. It can be reconverted by boiling with water.

Ferulic Acid, $C_{10}H_{10}O_4$, occurs as an ester in the resins c *Pinus Laricis*, asafœtida, and opoponax. It can be isolated fro asafœtida by mixing the alcoholic solution with an alcoholi solution of lead acetate. Lead ferulate is precipitated, whic

is decomposed by means of dilute sulphuric acid not in excess, the watery liquid is decolorised with animal charcoal and the acid and the crystalline residue taken up with hot alcohol and allowed to crystallise out.

Ferulic acid is related to *methyl-umbellic* acid, the lactone or anhydride of which, "*umbelliferone*," "*hydroxycoumarin*," occurs in asafœtida and galbanum resins and in the bark of the *Daphne mezereum*.

Aromatic Balsams.

The aromatic "balsams" are such of the oleo-resinous exudations of plants as contain benzoic or cinnamic acid, and yield cinnamic or benzoic methyl or ethyl esters by dry distillation. The term "balsam" is misapplied to "Canada balsam" and "copaiba balsam," which are true turpentines and do not contain or yield benzoic or cinnamic acid.

The aromatic balsams of practical interest are gum benzoin; Peruvian balsam; Tolu balsam; and liquid storax. The first of these will be conveniently considered separately, and the others conjointly under the head of "Cinnamic Balsams."

GUM BENZOIN. Gum Benjamin. The greater part of the benzoin of commerce comes from the *Styrax benzoin*, a tree of the East Indies. Several varieties of the balsam are known of which the more important are:—Siam and Sumatra benzoin (from the *S. benzoin*); Penang benzoin (probably from the *S. subdenticulata*); Palembang benzoin (source uncertain, but not from *S. benzoin*); Padang benzoin (source uncertain).

Siam benzoin is the finest variety and occurs in tears, or masses consisting of loosely agglutinated tears, yellow, reddish, or brown externally, and translucent, milk-white, or almond-like internally. It sometimes occurs in brownish lumps, which when broken present an amygdaloid appearance from the white tears imbedded in the darker resinous matter. Siam benzoin melts at 75° C. This variety is never enveloped in cotton cloth.

Sumatra benzoin has a weaker and less agreeable odor than that of Siam. It occurs in large rectangular blocks, marked with the impression of a mat and covered with a white linen cloth. When broken, few but large white tears are seen in it. It is generally composed of brown resiniform matter with numerous small white chips or pieces intermixed, which give it a granitoid appearance. The white portions melt at 85° and the darker portions at 95° C.

Penang benzoin closely resembles the Sumatra variety, but occasionally differs from it in color, and more so in odor, which then suggests that of storax.

Gum benzoin always contains more or less bark and similar matters, and in inferior specimens these are present in very large proportion. With the exception of these impurities, benzoin should dissolve in five times its weight of alcohol. The resultant tincture from Siam benzoin has a distinct red color, while that yielded by the other varieties is brown or yellowish-brown. On addition of water, the liquid becomes milky, and the odour peculiar to the particular variety is readily perceived. That of Siam benzoin is pleasantly balsamic and similar to vanilla; Penang benzoin often smells like storax; while the odour of Sumatra benzoin is fainter, less pleasant, and distinct from either of the former.

The presence of cinnamic acid may be recognised by the odour of benzoic aldehyde (bitter-almond oil), developed on adding potassium permanganate to the hot liquid obtained by boiling the benzoin with milk of lime and filtering. Or the tincture of benzoin may be treated with water, and the liquid filtered from the precipitated resin treated with solution of permanganate or bleaching powder. Another method is to triturate the benzoin with lead dioxide and distil the mixture with water.

Cinnamic acid, indicated by the production of an odour of benzoic aldehyde on heating the benzoin with chromic acid mixture, is said by Muter to be characteristic of the Sumatra product. He gives as specially distinctive characters of Siam benzoin—the production of a cherry-red benzoin when sulphuric acid is added to the residue left on evaporating the solution of the benzoin in petroleum spirit; the complete solubility of the sample in chloroform but not in ether; and the lower melting point.

The determination of the cinnamic acid may be approximately effected as indicated on page 56. As much as 11 per cent. has been found.

Gum benzoin often contains from 12 to 14 per cent. of benzoic acid, but occasionally 18 or 20 per cent. is reached. The proportion present may be ascertained by the following sublimation process:—The sample is powdered, mixed with sand, and the mixture heated in a beaker or earthenware jar, furnished with a cap of thin filter-paper pierced with small holes. Over this is placed a cone or hood of stout paper. The benzoic acid sublimes and condenses on the inside of the hood, any oil and impurities being retained by the diaphragm of filter-paper.

Another method for the approximate assay of gum benzoin is to digest 10 parts of the powdered gum with 6 parts of slaked lime and 100 parts of water. After six hours, the liquid is boiled, filtered, and the residue washed. The filtrate is concentrated, rendered strongly acid with hydrochloric acid, and thoroughly cooled. The precipitated benzoic acid is filtered off,

washed with a little cold water, and dried between folds of blotting-paper. The small quantity of acid retained in the mother liquor may be extracted by agitation with chloroform, and the residue left by the spontaneous evaporation of the chloroform may be added to the main quantity of benzoic acid. A preferable plan is to agitate the acidulated liquid at once with chloroform, without filtering off the precipitated benzoic acid, and to subsequently recover the benzoic acid from its chloroformic solution by the spontaneous evaporation of the solvent, assisted by a current of dry air from a bellows. If ether be substituted for the chloroform the product will contain a small quantity of water and the determination will be too high. In any case, the benzoic acid extracted by chloroform or ether from Siam benzoin will be liable to contain vanillin.

Siam benzoin is mostly composed of a mixture of benzoresinol-benzoate and siaresinotannol benzoate, the latter being the more abundant. Among other ingredients are cinnamyl benzoate, or benzyl benzoate (0.3 per cent.), vanillin (0.15 per cent.), free benzoic acid, which may be as high as 15 per cent., and a small amount of impurities. As a rule cinnamic acid or cinnamic esters do not occur in Siam benzoin, which fact serves to distinguish it from the Sumatra and Panang sorts; but some observers report samples of Siam benzoin in which cinnamic acid or its esters exist.

Sumatra benzoin. This consists principally of a mixture of benzoresinol cinnamate and benzoresinotannol cinnamate. The remaining ingredients are free benzoic acid, styrol, traces of benzaldehyde, benzene, vanillin 1 per cent., phenylpropyl cinnamate (about 1 per cent.), cinnyl cinnamate (styracin) (2–3 per cent.).

Palambang benzoin appears to be in the main similar to Siam benzoin in composition.

Padang benzoin. The composition of this is not well made out, but it seems to contain no cinnamic acid or ester thereof.

Penang benzoin contains cinnamic esters.

K. Dieterich (*Anal. d. Harze*, etc.) has devised a process applicable to benzoins in the commercial condition. This includes the determination of ash and of data termed respectively "indirect acid number," "cold-saponification number," and "ester number." The last datum is derived from the first two. The procedures are as follows: The weighed portions should be taken from a comparatively large amount of the material that has been finely powdered and well mixed.

Indirect acid number. 1 gram is mixed in a flask with 10 c.c. of half normal alcoholic alkali and 50 c.c. of 96 per cent. alcohol. The mixture is allowed to stand exactly 5 minutes, and then titrated with half normal sulphuric acid and phenolphthalein

until the solution is yellow, and a fresh portion of the indicator does not turn red on being dropped into the liquid, and the sodium sulphate separates readily. The supernatant liquid must be yellow. The c.c. of alkali neutralised by the sample, multiplied by the 28.08, gives the *acid number*.

Cold-saponification number. 1 gram of the sample is placed in a glass-stoppered flask with 20 c.c. of half normal alcoholic alkali and 50 c.c. of petroleum spirit (sp. gr. 0.700). The flask, tightly closed, is allowed to stand for 24 hours at room temperature; after dilution with alcohol, the liquid is titrated with half-normal sulphuric acid and phenolphthalein. The c.c. of alkali neutralized, multiplied by 28.08, gives the cold-saponification number.

The *ester number* is the difference between the above data.

Dieterich gives the following as the limits of data on pure samples of the different benzoins:—

	Siam.	Sumatra.	Palambang.	Padang.	Penang.
Ash	0.03–1.5	0.0–1.5	1.1–4.02	1.07	0.38–0.77
Ind. A-N	140–170	100–130	113.4–130.9	121.8–124.6	121.8–137.2
Cold-S-N	220–240	180–230	198–219.8	201.6–205.8	210–296.8
E-N	50–75	65–125	84–91	79.8–812	87.5–91.7
Sol. in 96% alcohol	95%	70–80%	91%		94%

Dieterich found that the above data are more or less influenced by several of the usual adulterations of benzoin. Dammar and storax depress the acid number; turpentine depresses the cold-saponification and ester numbers; colophony depresses the acid number, but the effect is noticeable only when comparatively large amounts are present. For special tests for colophony, see under that substance.

The United States Pharmacopœia (1900–1905, 8th Decennial Rev.) makes no specific distinction of the varieties of benzoin, but mentions Siam and Sumatra benzoin. The official article is required to dissolve almost wholly in five times its weight of warm alcohol (95 per cent. by volume), the solution being acid to litmus. It must be entirely soluble in solution of potassium hydroxide or sodium hydroxide and must not contain more than 2 per cent. of ash.

The *Helfenberger Annalen* for 1903 (quoted by *Chem. and Drug.*, 1904) gives the following data from a sample of Siam benzoin, but the details of the methods used are not available:

Acid value	**126.2**
Ester value	**96.4 – 95.0**
Saponification value	**221.2–222.6**
Ash	**0.27 per cent.**
Insoluble in spirit	**3.6 "**

Tincture of Benzoin. This is a simple solution of benzoin in alcohol of about 95 per cent.; usually the proportion is 1 of benzoin to 5 of alcohol. Compound tinctures are also used. The assay of these preparations is not much understood. For the compound tincture prepared according to the British Pharmacopœia it has been claimed that it will be of such strength that 10 c.c. will leave not less than 1.8 grams of residue on evaporation. Owing to the volatility of some of the ingredients, it is difficult to evaporate to constant weight. E. Dowzard (*Chem. and Drug.*, February 20, 1904) states that the following process will give good results:

Two c.c. of the sample are placed in a tared flat-bottomed nickel basin (diameter about 6 cm.); to this 0.1 gram of recently ignited magnesium oxide in fine powder is added; the mixture is worked into a smooth condition with a small glass rod, which should be weighed with the basin. After allowing the mixture to stand for about fifteen minutes, the alcohol is slowly driven off, stirring continually. The basin is then placed in a water-oven, and its contents dried at 99°–100° C. for four or five hours. For drying purposes Dowzard uses an oven through which a slow current of dry air passes, a high vacuum being at the same time maintained. If an ordinary drying-oven is used a longer time will be required than when using a vacuum apparatus. Before taking out of the oven, a cap of filter-paper perforated with small holes should be placed over the basin as crepitation occurs on cooling. If after the first weighing a further drying is considered necessary, the perforated cap should be put over the basin before it is placed in the oven. and should not be removed until the moment before weighing; if this precaution is not taken a slight loss may occur.

The weight of magnesium oxide used must of course be subtracted from the result. The benzoic and cinnamic acids are part of the total solids, and most important constituents of the tincture; they should therefore be fixed by chemical means before drying.

A large batch of this tincture, made on the manufacturing scale, was found to contain 19.4 grams of extractive per 100 c.c. when tested by the above method, using magnesium oxide as a fixing agent. If the extractive from compound tincture of benzoin is dried to a constant weight at 100° C., the results will be from 2 per cent. to 2.5 per cent. below the actual amount of total solids present.

Cinnamic Balsams.

Under this description are included Peruvian balsam, Tolu balsam, and liquid storax. These substances are all closely allied

to one another, but in their physical properties and quantitative chemical composition, they present considerable differences.

The following table exhibits the more important distinctions between Peru and Tolu balsams and storax:—

	Peruvian Balsam.	Tolu Balsam.	Liquid Storax.
Botanical origin	*Toluifera Pereiræ.*	*Toluifera Balsamum.*	*Liquidambar orientalis.*
Geographical origin..	San Salvador, Central America.	Colombia, Turbace, Tolu, and Venezuela.	Asia Minor.
Consistency and appearance.........	Viscid, but not glutinous, dark-brown liquid, resembling molasses; transparent and reddish-brown in thin layers. Gradually thickens on exposure.	When fresh, yellow, transparent, and liquid; changing rapidly to reddish-brown, and becoming solid and friable, or brittle; but softening between the teeth, and readily fusing. Such samples have a granular crystalline structure; and crystals of cinnamic acid are visible under the microscope.	Brownish-yellow or greyish, viscous liquid. Under the microscope shows globules of water, tabular crystals of cinnamic acid, and frequently feathers of styracin.
Taste.............	Bitter and persistently irritating.	Sweetish, aromatic, and somewhat irritating.	Pungent and balsamic.
Odor.............	Agreeable.	Aromatic; more apparent on warming.	Sweetish or strong and oppressive.

Peruvian Balsam is readily soluble in all proportions in absolute alcohol, glacial acetic acid, chloroform, acetone, and ethyl acetate; with an equal bulk of alcohol and ether it yields a clear solution, which on further addition of the solvent becomes turbid and deposits resin. Diluted alcohol takes up only a small proportion of the balsam. Cold ether and petroleum spirit dissolve it partially.

Cold petroleum spirit only dissolves the cinnamein and cinnamic acid of the balsam, but on employing the hot solvent styracin is also dissolved, and is deposited in crystals on cooling. Carbon disulphide acts in a characteristic manner. Agitated with three times its weight of the cold solvent, the greater part of the balsam is dissolved to a colourless or slightly coloured liquid, from 10 to 16 per cent. remaining as a reddish-brown, sticky liquid, adhering firmly to the sides of the glass, while the solution may be readily poured off.

The cinnamic balsams are closely allied, consisting essentially of the benzyl and cinnamyl ethers of benzoic and cinnamic acids, mixed with resinous oxidation products of these ethers, free

benzoic and cinnamic acids, and the hydrocarbon cinnamene. The leading or characteristic constituents of Peru balsam may be said to be the cinnamein or benzyl cinnamate and styracin or cinnamyl cinnamate. Free benzyl alcohol is also present. In Tolu balsam, on the other hand, the proportion of resin is large; but of the ethers benzyl benzoate predominates, and cinnamyl benzoate and cinnamate exist in but small proportions. In liquid storax of Mexican origin, phenylpropyl cinnamate exists in considerable quantity; two isomeric alcohol-like bodies called α- and β-storesinol, to which the formula $C_{36}H_{55}.(OH)_3$ is attributed (*Ber.*, **9**, 274); and the cinnamic ethers of these bodies.

In some cases the substances obtained from the cinnamic balsams have been decomposition products of the methods of analysis. The following method may be adopted for the recognition of the principal constituents of aromatic balsams:—The substance is dissolved in two or three parts of ether, and filtered from any insoluble matter. The solution is agitated with an equal measure of normal sodium hydroxide, the alkaline liquid withdrawn, and the agitation repeated with a fresh quantity of solution. If desired, the total acidity of the balsam can be deduced from the titration of an aliquot part of the alkaline liquid. The ethereal layer is then washed with water, and distilled at a gentle heat, the residue of neutral ethers, etc., being weighed. The residue is then fractionally distilled.

The first fraction will contain any *cinnamene* which may be present, the next being rich in *benzyl alcohol*, which may be extracted by agitation with water and will yield benzoic aldehyde and acid by oxidation. *Cinnamyl alcohol* and *benzyl benzoate* pass over next, and at a higher temperature *benzyl cinnamate* and *cinnamyl benzoate* and *cinnamate* may be obtained. These ethers suffer more or less decomposition unless the distillation is conducted *in vacuo*, and hence the last fractions consist largely of cinnamic acid, which can be removed by agitating the distillate with sodium carbonate solution. The alkaline liquid separated from the ethereal solution should be saturated with carbon dioxide, which precipitates much *resin*. The liquid is filtered, concentrated, and treated with hydrochloric acid, when a bulky precipitate is obtained representing the *free benzoic* and *cinnamic acids* of the balsam. These bodies may be identified by their ordinary reactions. For their approximate separation, one-half of the precipitate may be boiled with milk of lime and the liquid filtered and allowed to become cold, when the sparingly soluble calcium cinnamate is deposited in shining needles, the more soluble benzoate remaining in solution. The methods indicated on page 40 may also be utilised for the separation of

the two acids. When an exact determination of the free acids of a balsam is desired, it is better to agitate the ethereal solution with sodium carbonate instead of sodium hydroxide, as the latter reagent is liable to cause some decomposition of the ethers.

Except for purposes of research, it is rarely necessary to make such an analysis of a balsam as is indicated above.

Adulterations of Peruvian Balsam.

Peruvian balsam is liable to adulteration with the cheaper cinnamic balsams (Tolu and storax); copaiba and gurjun balsams; colophony; an alcoholic solution or extract of gum benzoin; alcohol; and even with fixed oils, especially castor oil. Hence the examination of Peru balsam for the detection of these adulterants is of some importance. Many of the usual adulterants of balsam have a lower specific gravity than the genuine substance, which varies in density between very narrow limits, 1.150 being the maximum and 1.137 the extreme minimum. Any sample having a lower density than 1.138 should be regarded with suspicion.

The presence of *alcohol* is indicated by the loss of volume undergone by the balsam on agitating with water. Small quantities may be detected by distilling the sample with water and sodium carbonate and examining the distillate by the iodoform and chromic acid tests.

The investigations of Dieterich (*Anal. d. Harze.*, etc.) have shown that many of the commonly accepted tests for purity of this balsam have no value. He gives the following data as of service:—

Direct Acid Number. 1 gram of the sample is dissolved in 200 c.c. of alcohol (96 per cent.) and titrated with decinormal alcoholic alkali, using phenolphthalein. The c.c. of alkali required multiplied by 5.616 gives the direct acid number.

Cold Saponification Number. The procedure is mainly as given under "Benzoin," using 1 gram of the sample in a 500 c.c. glass-stoppered flask with 50 c.c. of petroleum spirit (sp. grav. 0.700) and 50 c.c. half-normal alcoholic alkali. After standing twenty-four hours at room temperature, 300 c.c. of water is added, well shaken, until the separated dark alkali salt has been dissolved and the solution titrated, with continuous agitation, with half-normal sulphuric acid, with phenolphthalein. The c.c. of alkali neutralised by the sample, multiplied by 28.08, gives the cold saponification number.

The *ester number* is obtained by subtracting the direct acid number from the cold saponification number.

Ether insoluble matter. This is obtained by Dieterich by adding warm ether in small portions to a weighed portion of the sample until a portion of the solvent no longer leaves any residue on evaporation. The undissolved portion is then weighed. It will probably be better to extract in the regular Szombathy (so-called Sohxlet) tube.

Aromatic and volatile ingredients. The ethereal extract is shaken with 20 c.c. of a 2 per cent. sodium hydroxide solution, separated and evaporated in room temperature until no odor of ether is perceptible. The residue is placed for twelve hours in the desiccator, weighed, placed for a second twelve hours in the same and weighed again. The mean between these two weights is taken as the datum for fixed matter from which the volatile matter can be calculated.

Esters of Resin-acids. The alkaline solution separated from ether by the action of the alkali, as noted in the last paragraph, is rendered acid by dilute hydrochloric acid, filtered through a tared filter, washed by the aid of filter pump, with as little water as possible until the washings are free from chlorides. The residue dried at 80° to constant weight is taken.

With these processes, Dieterich obtained from commercial samples the following range of data:—

Sp. gr.	1.135	1.145
Direct acid number	60	80
Cold saponification number	240	270
Ester number	180	200
Resin esters	20	28
Aromatic and volatile ingredients	65	77
Ether insoluble	1.5	4.5

From authentic pure specimens from Honduras the following figures were obtained:—

	I.	II.	III.
Direct acid number	77.4	76.9	77.3
Cold saponification number	243.0	214.3	215.0
Ester number	165.6	137.4	137.6
Resin esters	15.7	13.8	17.3
Aromatic and volatile ingredients	71.4	77.5	73.6
Ether insoluble	4.3	4.3	3.5

The conclusions are:—

Adulterations usually raise the direct acid number and lower the cold saponification number.

A low ester-number indicates adulteration; if below 100 it suggests colophony, Tolu balsam, or benzoin.

The matter insoluble in ether has a sorting value but is of no use in detecting common adulterations.

In commercial samples the proportion of cinnamein ranged from 65–75 per cent., and of resin esters 20–28 per cent., that is, a ratio of 1 of the latter to 3 of the former. Ratios, therefore, of 1 to 2 or 1 to 5 indicate much adulteration.

In valuing a sample, a high content of cinnamein is preferable to high content of resin-esters.

Tolu Balsam. This is from a leguminous plant, *Myroxylon Toluifera,* growing in the northern portion of South America. In fresh condition the balsam is brownish yellow, transparent in thin layers and non-crystalline, but in time becomes hard, crystalline and darker. The odor is aromatic and pungent. The melting-point ranges from 60°–65° C. It dissolves in alcohol, chloroform and in watery solutions of alkalies. The alcoholic solution is acid to litmus.

The constituents of Tolu balsam are not fully known, but it appears to consist principally of the following ingredients:—

(1) An oily portion, benzyl benzoate with a little benzyl cinnamate; (2) cinnamic and benzoic acids; (3) vanillin; (4) toluresinotannol benzoate and cinnamate. Of these (4) is the most abundant; (1) forms about 7 per cent.; (2) from 12–15 per cent.; (3) only traces. About 3 per cent. of impurities of various kinds are present.

By steam distillation on a large scale, a small amount of a volatile oil of pleasant odor can be obtained. This has sp. gr. ranging from 0.945 to 1.090, slight optical activity, sometimes positive, sometimes negative, and contains phellandrene.

Adulteration of Tolu Balsam.

The common adulterant is colophony, but exceptionally when the balsam is high in price other substances (*e. g.,* copaiva) may be used.

For the detection of colophony qualitatively the Storch-Morawsky test (see under "Colophony") may be used.

The solubility in carbon disulphide has been proposed as a test and in the British Pharmacopœia of 1898 is given as follows:—

5 grms. of the sample are extracted with 25 c.c. and then 10 c.c. of warm carbon disulphide. Upon evaporating the mixed solutions, the residue should require not less than one-third of its weight of potassium hydroxide for saponification, thus indicating a sufficient amount or cinnamic and benzoic acids in the sample.

Some good authorities are, however, not inclined to rely on

this test, and much further study of this balsam is needed. K. Dieterich says that little if any pure Tolu balsam is in the market. He gives the following data obtained by E. Dieterich, with which his own figures correspond, but the latter are not specially quoted:—

Direct acid number	115.8–158.6
Saponification number	155.3–187.4
Ester number	31.2 40.5

Solubility:

Alcohol (90 %)	wholly soluble.
Ethyl acetate	wholly soluble.
Chloroform	almost wholly soluble.
Ether	53.2–87.9 %.
Benzene	82.2–nearly 100 %.
Petroleum spirit	2.2–10.2
Oil of turpentine	27.8–54.5
Carbon disulphide	19.6–88.1

LIQUID STORAX.

This is the product of *Liquidambar orientalis* of Asia Minor, and of *Liquidambar Styraciflua* of America. It is a brownish-yellow or greyish viscous liquid, the better qualities of which possess a sweet, vanilla-like odor. Inferior specimens contain impurities which render the odor oppressive and disagreeable. The taste is pungent and balsamic. Under the microscope globules of water and crystals of cinnamic acid and styracin are visible. When treated with strong alcohol, ether, or chloroform, liquid storax dissolves, but generally leaves some mechanical impurities. With an equal weight of warm alcohol it yields a turbid solution of acid reaction. The filtered liquid, when evaporated, yields not less than 70 per cent. of the original balsam, as a brown semisolid mass which constitutes "Prepared Storax." This is entirely soluble in ether and carbon disulphide and almost completely soluble in benzene, but is only partially soluble in cold petroleum spirit, more freely in hot petroleum spirit and the solution deposits crystals of cinnamic acid and styracin on cooling.

The residual pressings of the bark after obtaining the liquid storax are used under the name "*styrax calamitus.*" Mixtures of storax with an inert solid are also known by this name, and formerly the resin of *Styrax officinalis* was also known in commerce under this description.

Oriental Storax (from *Liquidambar orientalis*) contains styrol, $C_6H_5.CH:CH_2$, cinnamic acid, styracin (cinnamyl cinnamate), $C_9H_9C_9H_7O_2$), cinnamic acid, phenyl-propyl cinnamate, ethyl cin-

namate, vanillin, ethyl-vanillin; α- and β-storesin, $C_{35}H_{35}(OH)_3$, an amorphous resin, traces of benzoic acid and storesinol cinnamate. According to *Tschirch*, benzoic and cinnamic acids are never found in the same specimen of oriental storax.

Storesinol has the formula $C_{16}H_{25}O(OH)$, and its cinnamic ester is present to the extent of about 35 per cent. in the balsam.

American storax is known also as *sweet gum*, and according to Harrison and Maisch (*Archiv der Pharm.*, 1875, 545), it is identical with oriental storax; but this is improbable. It contains styracin, phenyl-propyl cinnamate and storesin; but not ethyl or benzyl cinnamate. Styrol and traces of vanillin are probably present.

The commoner adulterants of storax are turpentine rosin, castor oil, olive oil and similar fatty oils. Ladanum resin has been found by K. Dieterich.

Samples of crude storax have been examined chiefly by continental chemists, and the following figures, compiled from their results, represent a wide scope:—

	Acid Number.	Ester Number.	Saponification Number.
Beckurts and Brüche[1]	68–93	112–153	180–222
A. Kremel[2]	47.6	31.9	79.5
E. Dieterich	37.2–96.7	74.6–168	134.6–249
K. Dieterich[3]	57.5–59.4	—	—
Evers	52.2–56.7	173.5–184.2	230.2–236.4

[1] 6 samples of authentic origin.
[2] A sample adulterated with turpentine.
[3] 2 pure samples.

K. Dieterich has further examined a number of commercial and absolutely authentic samples, and gives the following comparative results:—

	Authentic.	Commercial.
Water, %	26.21 – 40.97	19.58 – 31.95
Ash	0.5 – 0.92	0.24 – 3.64
Soluble in alcohol (after deducting water)	57.14 – 65.49	64.90 – 77.17
Acid number	59.38 – 70.70	38.22 – 72.29
Ester number	35.42 – 74.43	47.81–110.03
Saponification number	104.67–135.36	111.89–187.76

E. Dieterich gives the following table of solubilities:—

	Per Cent.
90 % alcohol	56.14–84.00
Acetic ether	69.40–73.60
Chloroform	69.20–72.60
Ether	65.80–82.80
Benzene	64.80–74.80
Turpentine	54.40–57.80
Carbon bisulphide	62.30–67.80
Petroleum spirit	15.00–19.40

The specific gravity should lie between 1.113 and 1.121, according to Beckurts and Brüche, who also give the amount dissolved in an equal volume of pure alcohol as 61–71 %.

The following interesting table is given by K. Dieterich. Unfortunately, the figures for the pure storax are not given:—

Pure Storax with	Water.	Ash.	Soluble in Alcohol (after Deducting Water).	Acid No.	Ester No.	Saponification No.
20 % olive oil	33.73	0.62	63.87	53.65	72.98	126.63
30 % " "	28.22	0.47	70.59	53.08	78.34	131.42
20 % castor "	33.96	0.51	64.72	57.21	66.84	124.05
30 % " "	29.30	0.33	69.65	51.31	79.88	131.19
20 % turpentine	39.56	0.61	59.30	78.40	29.53	107.93
30 % "	34.62	0.53	63.36	84.40	23.01	107.05

Soluble in petroleum ether	37.54–58.96
" in alcohol 90 %	practically entirely
" in ether	93.14–100
" in chloroform	almost entirely
" in acetic ether	entirely
" in benzene	95.75–100
" in turpentine	81.8 – 99.55
" in carbon bisulphide	86.8 – 93.39

The British Pharmacopœia (1898) only recognises "*Styrax Præparatus*," the product of *Liquidambar orientalis*, purified by solution in alcohol, filtration and evaporation of the solvent. It requires it to give off no moisture on heating and to evolve an odor of essential oil of bitter almonds when boiled with sulphuric acid and solution of potassium bichromate.

Resinous adulterants in Storax. Ahrens and Hett (*Zeit. Ang. Chem.*, 1903, 384; also *Pharm. Jour.*, **73**, 1904, 547) find that storax adulterated with rosin yields to light petroleum spirit from 55.1 to 63.7 per cent. of extract; this has an acid value between 116.3 and 120.9, and a cold saponification value between 171.6 and 177.6. Specimens of pure storax of recent and older importation gave a light petroleum spirit extract of 37.6 to 47.6

per cent., with an acid value ranging from 37.6 to 47.6 and a saponification value (cold) of 194.6 to 198.4. Adulteration with rosin is more readily detected by this method of separating and treating the light petroleum spirit extract than by determining the saponification constants of the original drug, as recommended by Dieterich.

SALICYLIC ACID AND ITS ALLIES.

Salicylic acid is the type of a group of compounds containing the radical hydroxyphenyl, $C_6H_4(OH)$, and has itself the constitution of a hydroxyphenyl-carboxylic acid, $C_6H_4(OH).COOH$. Thus it may be regarded as a hydroxy-benzoic acid, and as the hydroxyl and carboxyl groups occupy adjacent positions in the benzene-nucleus, salicylic acid is the *ortho-* form of the acid, all three modifications of which are known. The fact that two of the hydrogen atoms of the benzene-nucleus are replaced, renders all the compounds of the group capable of existing in ortho-, meta-, and para-modifications. In the case of the homologues of the hydroxybenzoic acids, where a third substitution of hydrogen by methyl or other alkyl-radical occurs, the number of possible isomers is still further increased.

Isomeric Hydroxybenzoic Acids.

The table on page 64 exhibits the characteristics of the three isomeric acids.

Salicylic acid and methyl salicylate occur in many plants. Para-hydroxybenzoic acid has been found in the pods of *Bignonia catalpa*.

When salicylic acid is heated to 195° to 220° it is, according to Graebe and Eichengrün (*Annalen*, cclxix, 323), to a great extent converted into phenyl salicylate, and if the product is distilled, a considerable quantity of xanthone is formed. On the other hand, if *para*-hydroxybenzoic acid is heated in an open dish to 200°, phenol and carbon dioxide are the chief products, and there finally remains only a very small quantity of some compound of high melting-point. *Meta*-hydroxybenzoic acid undergoes very little change even on prolonged heating to 210°.

Salicylic acid prevents the precipitation of cupric salts by alkalies, but its isomers have not this property.

Meta- and para-hydroxybenzoic acids are liable to be present in commercial salicylic acid (see page 78, *et seq.*).

The following table exhibits the leading differences between the three isomeric hydroxybenzoic acids:—

	Ortho-Acid (*Salicylic Acid*).	Meta-Acid.	Para-Acid.
Formula,	$C_6H_4\begin{cases}OH(^1)\\COOH(^2)\end{cases}$	$C_6H_4\begin{cases}OH(^1)\\COOH(^3)\end{cases}$	$C_6H_4\begin{cases}OH(^1)\\COOH(^4)\end{cases}$
Specific gravity at 4° C. (Schröder),	1.4835.	1.473.	1.468.
Melting-point,	156.7° C.	200° C.	210° C.
Solubility:			
In Water at 0° C.,	1 in 1100.[1]	1 in 265.	1 in 580.
" " 15° to 18°,	1 in 1000.	1 in 108.	1 in 126.
In Chloroform,	Readily soluble.	Almost insoluble.	Very slightly soluble.
Reaction with Ferric Chloride,	Deep violet colour.	No change.	Yellow flocc. ppt. sol. in excess.
Reaction when heated in a current of dry Ammonia Gas,	Yields Phenol, CO_2, etc.	Yields hydroxybenzonitrile, $C_6H_4(OH)CN$, melting at 82° C.	Yields phenol, CO_2, etc.
Products with Bromine-water in excess,	$C_6H_2Br_3.OBr + CO_2$.	$C_6HBr_3(OBr).COOH$.	$C_6H_2Br_3.OBr + CO_2$.
Antiseptic properties,	Strong.	None.	Doubtful.

Salicylic Acid. Ortho-hydroxybenzoic Acid.

$$C_7H_6O_3;\ \text{or},\ C_6H_4\begin{cases}OH\\COOH\end{cases}.$$

Salicylic acid is the only modification of the three isomeric hydroxybenzoic acids of any importance. It bears the same relation to benzoic acid that glycollic acid does to acetic acid. Salicylic acid was originally prepared from salicin, $C_{13}H_{18}O_7$, a bitter glucoside existing in willow-bark,[2] but is now chiefly made synthetically from phenol. It may also be prepared from

[1] According to Bourgoin (*Jour. Pharm. Chimie*, [4], xxx, 488), the solubility of salicylic acid at 0° C. is 1 part in 666, instead of the number given in the text, which is due to Ost (*Jour. Prac. Chem.*, [2], xvii, 228).

[2] Salicylic acid was obtained in 1838 by Piria, who prepared it by the oxidation of salicylic aldehyde (from salicin) by fusing with caustic potash (*Annalen*, xxx, 165). In 1843, Cahours proved that oil of wintergreen consisted almost entirely of methyl salicylate. In 1853, Gerland showed that anthranilic acid could be converted into salicylic acid by reaction with nitrous acid, and in 1860, Kolbe and Lautemann prepared salicylic acid synthetically from phenol, sodium, and carbon dioxide.

oil of wintergreen (*Gaultheria procumbens*) or oil of sweet birch (*Betula lenta*), but this so-called "natural" acid is far more expensive than the artificially prepared substance. The chief advantage claimed for the natural acid is its freedom from the isomeric para-hydroxy acid, which is liable to be present in carelessly-made artificial salicylic acid and is by no means harmless in its physiological effects. Practically the whole of the acid of commerce is now prepared by a method discovered by Kolbe, which is based on the action of carbon dioxide on sodium phenate.[1]

When potassium phenate is heated in a stream of carbon dioxide, it is acted on in a manner similar to sodium phenate in Kolbe's process, yielding pure di-potassium salicylate up to 150°; but above that temperature the isomeric para-hydroxybenzoate is also produced, and at 220° is the sole product.[2] The same body is formed if the caustic soda employed in Kolbe's

[1] Crude soda lye of known strength is exactly saturated by crystallised carbolic acid, and the liquid cautiously evaporated till the residue is perfectly dry. It is then subjected to the action of a stream of carbon dioxide gas at a temperature commencing at 100° C., which is gradually raised to 180°, and may reach 220° or 230° C. towards the close of the operation. During this process, phenol distils over and ultimately amounts to about half the quantity taken. The residue in the retort consists of basic sodium salicylate, the solution of which on fractional precipitation with hydrochloric acid yields impure salicylic acid. The first portions thrown down are contaminated with resinous and colouring matters, and are rejected. The remainder of the precipitate is washed, recrystallised from hot water, and distilled at 170° C. in a current of superheated steam, when the acid is obtained perfectly white. If carbolic acid containing cresylic acid be used in Kolbe's process, the product contains cresotic acid (see page 104), which possesses many of the properties of salicylic acid; but for internal medicinal use pure salicylic acid should be employed.

The reaction between sodium phenate and carbon dioxide in the cold results in their direct union with formation of sodium phenylcarbonate, $(C_6H_5)O.CO.ONa$, a white powder decomposed by water into phenol and sodium hydrogen carbonate. On heating this compound to 130° it undergoes direct molecular transformation into mono-sodium salicylate, $C_6H_4(OH).CO.ONa$. The formation of phenol and basic salicylate is due to the reaction of this salt at a high temperature with unchanged sodium phenate:—$C_6H_4(OH)CO.ONa + C_6H_5.ONa = C_6H_4(ONa).COONa + C_6H_5.OH$. A more advantageous reaction can be realised on a manufacturing scale by treating perfectly dry sodium phenate with the requisite quantity of carbon dioxide under pressure (either employing the gas or solid substance), the temperature being kept down artificially. On heating the product for several hours to 120°–130°, it is transformed into mono-sodium salicylate without separation of phenol. Operating in this manner salicylic acid can be obtained from half the quantities of soda and phenol which are required if Kolbe's process be followed.

[2] Mono-potassium salicylate is converted into the basic para hydroxybenzoate and phenol when heated to 220°, whereas the corresponding sodium salt yields the ortho-hydroxybenzoate or salicylate, together with phenol.

process contains potash, and, according to B. Fischer, it is also produced if the temperature be too low when the gas is passed. Too high a temperature is said by Fischer to cause hydroxy-isophthalic acid to be formed at that stage, owing to the action of the gas on the sodium salicylate already formed. In a well-conducted operation, para-hydroxybenzoic and hydroxy-isophthalic acids are not usually formed in quantities exceeding 0.4 per cent., and the former may be easily removed by washing, as it is readily soluble in water. Hydroxy-phthalic acid is less soluble, and may be present to the extent of 1 per cent. in some cases.[1]

If traces of iron compounds are present in the materials used in Kolbe's process, brown or yellow oxidation-products are formed which are insoluble in water, and give a yellow colour to the salicylic acid obtained.

Salicylic acid crystallises from alcohol in large monoclinic prisms. As met with in commerce the acid usually occurs as a granular powder, consisting of minute, broken, acicular crystals. It has a sweetish, acidulous, acrid taste. The specific gravity is 1.483 at 4° C.

The melting-point of salicylic acid has been stated by various observers at points ranging from 155° to 159° C., but Fischer finds the melting-point of the pure acid to be 156.75° (corrected), and this result has been confirmed by Dunstan and Bloch. Even a small proportion of the cresotic acids tends to lower the melting-point of the sample.

When gradually heated to about 200°, salicylic acid sublimes in slender shining needles, but when heated rapidly in admixture with powdered glass or sand, it is resolved into phenol and carbon dioxide. Salicylic acid distils readily in a current of steam at 60 to 80 pounds pressure, and even vaporises on boiling its aqueous solution.

[1] Hydroxy-isophthalic Acid, $C_6H_3(COOH)^1(COOH)^3(OH)^4$, is now rarely met with in commercial salicylic acid. It may be detected by distilling the suspected sample in a current of steam, when it remains in the still in the form of a light grey powder or small lumps. By dissolving it in hydrochloric acid and filtering the solution through charcoal, the acid may be obtained in slender, white needles melting with decomposition at 300° to 305° C.

Hydroxy-naphthoic Acid, $C_{10}H_6(OH).COOH$, is a body which bears the same relation to naphthalene that salicylic acid bears to benzene. It is produced by the action of carbon dioxide on perfectly dry sodium alpha-naphthol at 130°. It forms colourless acicular crystals melting at 185° C. and requiring 30,000 parts of cold water for solution. Its salts give a blue coloration with ferric chloride. The corresponding acid from beta-naphthol melts at 235° and gives a violet-black colour with ferric chloride. Both varieties of hydroxynaphthoic acid are said to be powerful antiseptics, retarding the putrefaction of blood and urine much more perfectly than salicylic acid (*Pharm. Jour.* [3], xviii, 537, 823).

Salicylic acid is very sparingly soluble in cold water, and only moderately soluble in boiling water. The determinations of its solubility by different observers vary greatly. According to the British Pharmacopœia (1898), the acid is soluble in about 550 parts of cold or 9 of boiling water, in 3½ of alcohol of 90 per cent. strength, in 2 parts of ether, in 55 of chloroform, and in 195 parts of glycerin. It is also readily soluble in carbon disulphide, and is dissolved by 80 parts of benzene. Salicylic acid may be conveniently crystallised from hot petroleum-spirit. Agitation with ether, chloroform, or carbon disulphide readily removes salicylic acid from its aqueous solutions. H. Taffe recommends a mixture of ether and petroleum-ether for this purpose.

The solubility of salicylic acid in cold water is greatly increased by the presence of various salts.[1]

When heated with water under pressure to 230° C., salicylic acid splits up into phenol and carbon dioxide:—$C_7H_6O_3 = C_6H_6O + CO_2$. On heating with concentrated hydrochloric or dilute sulphuric acid the change occurs at a lower temperature (140° to 150°).

The distillation of salicylic acid with excess of lime produces calcium carbonate and phenol.

Salicylic acid readily dissolves in aqueous alkalies to form a series of well-defined and crystallisable salts (page 82).

When treated in aqueous solution with excess of bromine-water, salicylic acid is decomposed according to the following equation:—$C_6H_4(OH).COOH + 4Br_2 = C_6H_2Br_3.OBr + 4HBr + CO_2$ (compare page 75).

When ingested, salicylic acid is eliminated by the kidneys, partly in an unchanged state and partly in the form of the so-called *salicyluric acid*, a body which really has the constitution of *salicyl-glycocine*, $[C_6H_4(OH)CO].HN.CH_2.COOH$. This compound crystallises in fine needles which are slightly soluble in water but readily in alcohol. It melts at 160°, and gives a violet coloration with ferric chloride. The barium salt forms prisms very slightly soluble in water. When heated with concentrated hydrochloric acid, salicyluric acid is hydrolysed to salicylic acid and glycocine (amido-acetic acid).

Salicylic acid and its salts and esters are used extensively in

[1] Mixed with 1 part potassium nitrate, it dissolves in 50 parts of cold water.
" 1½ parts ammonium citrate, dissolves in 60 parts of " "
" 2 parts sodium sulphite, dissolves in 50 parts of " "
" 2 parts sodium phosphate, dissolves in 50 parts of " "
" 2½ parts sodium phosphate, dissolves in 12½ parts of " "

Salicylic acid is very soluble in solutions of borax, a compound of the formula $Na(BO)2C_7H_5O_3$ being said to be formed. The liquid, which is stated to be more powerfully antiseptic than either of its components, soon undergoes decomposition.

medicine, especially as intestinal antiseptics and in the treatment of gout and rheumatism of the joints.

Salicylic acid and its derivatives are now extensively employed as domestic remedies without seeking medical advice, but the practice is not free from danger. Salicylic acid, even when pure, has distinct toxic properties, and its salts cause albuminuria. The free acid, dissolved in flexible collodion or in the form of ointment, is strongly caustic, and is employed as a corn-solvent.

Salicylic acid now finds an extensive application as a preservative of various articles of food, though its use for such purposes is strictly prohibited in France and some other countries.[1] Wine, beer, milk, lime- and lemon-juice, temperance beverages, and many other articles are treated with salicylic acid in quantities which are often largely in excess of those necessary to preserve them. Such a practice is strongly to be deprecated, as the habitual and unconscious ingestion of an antiseptic necessarily tends to impair the digestive processes.

The employment of salicylic acid for preserving milk is now far less common than the use of formalin or boric acid for that purpose. Wines and temperance beverages frequently contain considerable quantities of salicylic acid,[2] and it is also extensively used in jam-making, from 4 to 8 grains of the acid to the pound being sufficient to prevent fermentation indefinitely. Uncooked fruits, such as cherries, plums, etc., may be preserved by pressing them, treating every pound of the juice with 15 grains of salicylic acid, heating the juice, and after cooling adding it to the pressed fruit.

The addition of 1 gramme of salicylic acid to the litre preserves a 10 per cent. solution of tartaric acid perfectly; but a

[1] A Departmental Committee on Food Preservatives appointed in 1899 recommended that salicylic acid should not be used in greater proportion than one grain per pint in liquid food and one grain per pound in solid food, and that its presence should in all cases be declared; also that salicylic acid, in common with all other preservatives, should be prohibited in milk and in all dietetic preparations intended for invalids and infants (*Analyst*, 1901, 332). These recommendations have now (1906) resulted in the issue of a circular by the Local Government Board (England) urging the desirability of prosecutions being instituted against vendors of "preserved" milk, and stating that milk may be presumed to have been rendered injurious to health if found to contain more than one part of formaldehyde, or 57 parts of boric acid, per 100,000 parts.

[2] According to medical witnesses called to defend the use of salicylic acid for this purpose, its addition is absolutely necessary to preserve the wine, and cannot possibly be injurious to health. This evidence was given at the hearing of a summons at Liverpool (October, 1900) for selling ginger wine containing 13 grains of salicylic acid to the pint. The analyst stated that of 33 samples of ginger wine examined by him, none of the others contained more than 4 grains per pint. A member of the defendant's firm deposed that they had tried smaller quantities of salicylic acid as a preservative, but found that the wine went bad.

solution of citric acid of the same strength requires twice that amount. Salicylic acid is stated not to have a preserving action on a solution of sodium succinate.

When an aqueous solution of salicylic acid is kept for some time, a fungoid growth forms, and this gradually decomposes all the salicylic acid (F. E. Lott, *J. S. C. I.*, 1903, p. 198). The rate of decomposition was found to be increased by the addition of small amounts of ferric chloride, thus confirming the statement that the growth of many moulds is stimulated by dilute iron solutions.

Reactions and Determination of Salicylic Acid.

Concentrated sulphuric acid dissolves pure salicylic acid without colour, forming a sulphonic acid. Impure salicylic acid gives a yellowish-brown coloration.

By the action of cold concentrated nitric acid on salicylic acid nitro-salicylic acid is formed, but with fuming nitric acid picric acid results.

Bromine gives a reaction with salicylic acid indistinguishable from that produced by phenol, and the same is true of its behaviour with Millon's reagent.

Sodium amalgam gradually reduces salicylic acid, in a warm, slightly acidulated solution, to its aldehyde, recognisable by its odour (page 94).

Silver nitrate and lead acetate give white precipitates with neutral salicylates, but not with free salicylic acid. Salicylic acid is not precipitated by barium or calcium chlorides, and neutral salicylates only in strong solution. Neutral salicylates in not too dilute solution (1 per cent.) give a yellowish-brown precipitate with a solution of uranium acetate. When boiled with excess of baryta-water, salicylic acid is precipitated as a basic barium salt.

With a solution of cupric sulphate, salicylates and free salicylic acid give an emerald-green coloration, visible in 2000 parts of water and destroyed by ammonia or acids.

The solution of salicylic acid in two molecules of sodium hydroxide prevents the precipitation of $\frac{1}{2}$CuO by additional alkali.

Fehling's solution is reduced by salicylic acid, and under favourable circumstances may be employed for its determination.

On heating salicylic acid or one of its salts with methyl alcohol and sulphuric acid, methyl salicylate is formed, having an agreeable aromatic odour.[1]

[1] C. O. Curtman (*Jour. Chem. Soc.*, lii, 185) recommends the formation of methyl salicylate for the detection of salicylic acid in wine or beer. He directs that 4 c.c. of the liquid to be tested should be mixed with 2 c.c. of methyl alcohol (or failing this, ordinary alcohol), and then

Salicylic acid, by virtue of its phenolic nature, combines with formic aldehyde. On dissolving the acid in a little formaldehyde solution, evaporating the liquid nearly to dryness, and then adding *strong sulphuric acid, a compound is precipitated* which is at first practically colourless, but becomes red, while the solution acquires a magenta colour.

Jorissen has observed that when a solution of salicylic acid or a salicylate is treated with sodium nitrite and a little acetic acid, followed by a drop or two of copper sulphate solution, and the liquid boiled, a *blood-red colour is produced*, varying in intensity according to the amount of salicylic acid present. The test has been confirmed in the author's laboratory and found very delicate. No similar reaction is produced by benzoic, cinnamic, or tartaric acid.

The most delicate reaction for salicylic acid and soluble *salicylates is that with ferric salts, which produce a beautiful* violet colour even in extremely dilute solutions. The reaction is greatly more delicate (1 in 100,000) than that of phenol with ferric salts (1 in 3,000). The violet coloration is due to the formation of ferric salicylate, and is destroyed by alkalies with precipitation of reddish-brown ferric hydroxide. It is also destroyed by mineral acids or others capable of liberating salicylic acid.[1] Certain neutral salts, such as phosphates, tartrates, citrates and oxalates, also interfere more or less with the reaction. Hence before applying the ferric reagent in the possible presence of such interfering substances,—as, for instance, in testing wine, beer, milk, urine, lemon-juice, etc.,—the liquid should first be acidulated with sulphuric or phosphoric acid, and agitated with ether, chloroform, petroleum-spirit, or other solvent of salicylic acid.[2] Of these solvents, ether is apt to extract

2 c.c. of pure sulphuric acid cautiously added. The liquid is agitated, heated for two minutes, allowed to cool for ten minutes, and then heated just to boiling, when if salicylic acid were present, a distinct odour of wintergreen oil will be perceptible. With traces, it may be necessary to allow the liquid to cool again, and then heat a third time. In examining condensed milk, etc., by this process, the sample should be digested for some hours with dilute alcohol, and the filtered liquid concentrated and heated as above.

[1] Weiske has proposed to employ the above reaction in alkalimetry. On neutralising an acid solution to which a trace of salicylic acid and ferric chloride have been added, the violet colour becomes gradually more developed until neutrality is reached, when the liquid turns reddish-yellow. But Pagliani has shown that the amount of mineral acid required for the destruction of the violet colour varies greatly with the nature of the acid, and the dilution of the liquid, and hence salicylic acid is ill-suited for use as an indicator. This is in accord with the author's experience.

[2] When only very minute quantities of salicylic acid are to be sought for, the liquid should be rendered slightly alkaline with caustic soda, and concentrated before being acidified and shaken with ether.

traces of tartaric acid and tannin matters, and hence a mixture of ether with an equal measure of petroleum spirit is preferable.[1] The immiscible solvent having been separated, any notable quantity of salicylic acid will yield the violet coloration on adding ferric chloride and agitating. A more delicate method is to shake the ethereal liquid with dilute ammonia, separate, evaporate the ammoniacal liquid at a gentle heat, and test the residue of ammonium salicylate with ferric chloride or iron alum.

As a confirmatory test, the ethereal residue may be warmed with a drop or two of strong nitric acid, and excess of ammonia added. The few drops of liquid obtained are then heated with a thread of white wool free from grease, which will be dyed a bright yellow by the picric acid formed, if salicylic acid were present. M. Spica states that 0.001 milligramme of salicylic acid can thus be detected.

Before extracting salicylic acid from its acidulated solution by ether, etc., some operators subject the liquid to a preliminary treatment. Thus, in the case of milk, H. Pellet dilutes 200 c.c. of the sample with an equal measure of water, heats to 60° C., and adds 1 c.c. of acetic acid, and an excess of mercuric nitrate free from mercurous salt. Wine, beer, or urine may be treated with lead acetate, the filtered liquid precipitated with dilute sulphuric acid, and the liquid again filtered and shaken with ether.

In testing wine it must be borne in mind that minute traces of salicylic acid are liable to be present naturally, but these do not interfere provided that the quantity of the sample used for the test is not too large. By employing the German official method, according to which not more than 50 c.c. of the wine is acidulated and shaken with a mixture of equal volumes of ether and petroleum-spirit, this source of error is avoided. Da Silva states that when thus applied the test is sensitive to one part of salicylic acid in 200,000 parts of wine. Medicus recommends that the ethereal extract from 50 c.c. of wine should be treated with 10 c.c. of water before adding ferric chloride (*Chem. Centralb.*, ii, 28).

According to R. J. L. Schoepp (abst. *J.C.S.*, 1896, ii, 227), the ferric chloride reaction is yielded by some specimens of beer undoubtedly free from salicylic acid, owing to the presence of *maltol*, a body isolated by Brand from roasted malt. This substance, however, does not yield any characteristic reaction with Millon's reagent, with which salicylic acid gives a dark red coloration. Hence, Schoepp considers it necessary in examining beer to use both tests.

[1] Or the acidified liquid may be extracted with ether, the ethereal solution evaporated, and the residue taken up with petroleum-spirit, which will leave any traces of tannin, tartaric acid, oxalic acid, etc., insoluble.

The ferric chloride reaction may be employed for the approximate colorimetric *determination* of salicylic acid. When the operation is performed on the original liquid, instead of using an aqueous solution of salicylic acid as the standard of comparison, it is preferable in all cases to add a definite amount of salicylic acid to a liquid of the same kind as that in which the salicylic acid is to be determined. Thus milk should be compared with milk, beer with beer, and urine with urine, and the standard specimen submitted to the same treatment as the sample to be compared with it. But in all cases it is preferable to extract the salicylic acid with ether before applying the iron test, as many substances weaken the colour-reaction or suppress it entirely. The ferric chloride solution should be very dilute, and must be added gradually till the coloration no longer increases. With small quantities of salicylic acid an excess of ferric chloride destroys the coloration.[1]

The following method of applying the ferric chloride reaction to the determination of salicylic acid in organic liquids and in foods, described by S. Harvey (*Analyst*, 1903, p. 2), has given good results in the author's laboratory.[2] Standard solutions of pure salicylic acid are prepared, containing respectively 0.100 and 0.010 gramme of the acid per 100 c.c. The salicylic acid is suspended in water and dissolved by adding a slight excess of caustic soda solution, and the liquid then rendered neutral to phenol-phthalein by decinormal sulphuric acid. The solutions should be freshly made when required. The use of hydrochloric acid throughout the process should be avoided, as it seems to interfere with the coloration. A one per cent. solution of iron-alum is used to produce the violet coloration, which is purer and more stable than that obtained with ferric chloride.

[1] According to Fajans (*Chem. Zeit.*, xvii, 69), the colorimetric estimation of salicylic acid by means of ferric chloride cannot be carried out in the presence of phenols. Advantage may be taken, however, of the fact that the latter give no colour with a solution of ferric chloride in absolute alcohol. To determine salicylic acid, the suspected liquid is acidified and extracted with ether, the solvent being allowed to evaporate spontaneously. The residue is dissolved in 25 to 30 c.c. of absolute alcohol, introduced into a graduated tube, and mixed with a few drops of a 5 per cent. solution of ferric chloride in absolute alcohol, until the colour ceases to darken. In a similar tube the same amount of an alcoholic solution of salicylic acid (2 in 10,000) is taken, and then a sufficiency of ferric chloride solution. Finally the darker of the two mixtures is diluted with absolute alcohol until they both shew the same intensity of colour; the difference in volume is noted, and the amount of salicylic acid thus found. According to Fajans, by this process 1 part of salicylic acid in the presence of 800 parts of phenol may be accurately estimated.

[2] Pellet and de Grobert (*J. S. C. I.* 1902, p. 1416) have described a similar method. Harry and Mummery (*Analyst*, 1905, p. 124) have devised a modified process, by which the tannin-matters frequently present in the liquid under examination are successfully removed and a pure colour obtained.

The alum solution should be acidulated with a few drops of dilute sulphuric acid per 100 c.c.

The liquid under examination is acidified with sulphuric acid, and extracted with ether[1] as already described. Syrupy and strongly alcoholic liquids should be somewhat diluted before extraction with the solvent. Two successive shakings with ether are sufficient, and but little colouring-matter is dissolved. The separated solvent is next shaken with two successive quantities of water containing a known amount (5 c.c.) of decinormal caustic alkali, the aqueous liquid being separated, carefully neutralised, and diluted to 250 c.c. or 500 c.c.[2] A known volume of this liquid is withdrawn, diluted if necessary to 100 c.c., and 1 or 2 c.c. of the iron-alum solution added. The operation is conveniently carried out in Nessler glasses, a standard being obtained in the same way by using the weaker of the two solutions of salicylic acid described above. The maximum amount of salicylic acid capable of being compared by this colorimetric process is 0.001 gramme per 100 c.c., but less than this amount is preferable.

In the absence of other bodies of acid character, free salicylic acid can be accurately determined by titration with caustic alkali. Phenol-phthaleïn is the preferable indicator, but litmus may be used. One c.c. of decinormal alkali solution represents 0.0138 gramme of salicylic acid. Caustic baryta solution is preferable to potash or soda for titrating salicylic acid, as its use ensures the absence of carbonate. It is not essential that the sample should be wholly in solution before commencing the titration, but towards the end of the process any salicylic acid still remaining undissolved should be brought into solution by warming the liquid. The above method of titration is available in presence of phenol.

Salicylic acid existing in the form of metallic salicylates can also be determined by the foregoing titration method, provided the solution be first freely acidulated with dilute sulphuric acid, and the liberated salicylic acid then extracted by agitation with ether or other solvent as already described. After separating, the immiscible solvent should be shaken twice with small quantities of water to remove traces of mineral acid. The dissolved salicylic acid may then be recovered by cautious evaporation, but some loss by volatilisation is difficult to avoid. A preferable plan is to add a few drops of phenol-phthaleïn solution, and

[1] The author prefers to use a mixture of ether and petroleum-ether, as recommended by H. Taffe (p. 67), instead of ether alone.

[2] The use of distilled water throughout the process is imperative. The accuracy of the method is impaired by the presence of more than small amounts of saline matter in the solution to be compared, and the slightest alkalinity is fatal to success. The slight acidity due to the iron-alum solution is an advantage.

titrate with standard baryta-water, agitating between each addition. If desired, the immiscible solvent may then be separated from the neutral aqueous liquid, which may be evaporated, and the residual barium salicylate weighed or further examined.

The volatility of salicylic acid in a current of steam may be utilised for its separation from certain interfering substances, but the process is not to be recommended, as complete volatilisation is difficult to attain. The solution of the substance should be freely acidulated with phosphoric acid, and distilled to a low bulk, water being then added and the operation repeated several times, or until the fraction last obtained exhibits no acid reaction to phenol-phthaleïn. Phenol, benzoic acid, and the three isomeric cresotic acids behave similarly to salicylic acid; but meta- and para-hydroxybenzoic acids and hydroxy-isophthalic acid are not volatile with steam. When the distillation process is to be applied to wine or beer, the liquid should be rendered alkaline with soda, reduced to half its bulk by boiling, to drive off the alcohol, and then acidulated and distilled as described above. When only traces of salicylic acid are present, the distillate should be made alkaline and concentrated before acidulating and shaking with ether or applying other tests.

Messinger and Vortmann (*Ber.*, xxiii, p. 2753) propose to precipitate salicylic acid from its alkaline solutions, by iodine, as sodium di-iodosalicylic iodide, afterwards titrating the excess of iodine with sodium thiosulphate. The reaction takes place as follows:—

$$C_6H_4(OH).COONa + 3NaOH + 3I_2 = C_6H_2I_2(OI)COONa + 3NaI + 3H_2O.$$

W. Fresenius and Grünhut (*Zeit. anal. Chem.*, xxxviii, p. 292) have criticised the method adversely, but Messinger has shown that, under proper conditions, it gives accurate results (*Jour. prakt. Chem.*, lxi, p. 236).[1] The process is also applicable to the determination of phenol, thymol, and β-naphthol.

[1] F. B. Power considers the process fairly accurate. Too large an excess of alkali should not be used. He gives the following data for one of his experiments:—0.4782 gramme of bismuth salicylate was dissolved in hydrochloric acid, the bismuth precipitated by sodium hydroxide, the liquid filtered, and the filtrate made up to 250 c.c. 50 c.c. of this solution was neutralised in a stoppered bottle with sulphuric acid, and then 0.5 c.c. of a 10 per cent. solution of caustic soda added. The bottle was immersed in hot water, and when the contents were at 60° C., 31 c.c. of decinormal iodine solution was added, and the flask kept warm and occasionally shaken for a few minutes. The liquid was then cooled, acidified with sulphuric acid, filtered, and the precipitate washed with a little water. The filtrate required 15.1 c.c. of thiosulphate, showing that the iodine of 15.9 c.c. had been absorbed. As 1 c.c. of decinormal iodine corresponds to 0.0023 gramme of salicylic acid, this indicated 38.25 per cent. in the bismuth salt, against a calculated amount of 38.45 per cent.

Salicylic acid may be determined by observing the amount of bromine with which it reacts. Salicylic acid is sometimes stated to be converted by treatment with bromine into dibromo-salicylic acid, according to the reaction:—$C_6H_4(OH).COOH + 2Br_2 = C_6H_2Br_2(OH).COOH + 2HBr$. It is probable that this equation correctly represents the reaction which first occurs, but numerous experiments by the author and other observers prove that salicylic acid in aqueous solution ultimately reacts with six atoms of bromine ($3Br_2$), to form a *tri*brominated salicylic acid,[1] this subsequently splitting up into carbon dioxide and tribromophenol, according to the equation:—

$$C_7H_3Br_3O_3 = CO_2 + C_6H_3Br_3O.^{2}$$

Neither this change nor the conversion of the tribromophenol into the body $C_6H_2Br_3OBr$ by the excess of bromine affects the process, since the former reacts with six atoms of bromine and the latter is converted into tribromophenol on treatment with potassium iodide in acid solution:—

$$C_6H_2Br_3.OBr + 2HI = C_6H_2Br_3.OH + HBr + I_2.$$

Hence by treating salicylic acid with excess of bromine-water, adding potassium iodide, and titrating the liberated iodine with standard thiosulphate, the amount of bromine which entered into combination can be deduced, and from it the weight of salicylic acid present.

The process as carried out in the author's laboratory is as follows:—A known weight of the sample is dissolved in water (preferably with the aid of a little caustic soda) and a measure corresponding to about 0.100 gramme of salicylic acid diluted to about 100 c.c. with water in a stoppered bottle. 10 c.c. measure of hydrochloric acid (sp. gr. 1.1) is next added, followed by a known volume (about 50 to 60 c.c.) of a solution containing sodium bromate and bromide, of which sufficient should be used to give about 75 per cent. of bromine in excess of that entering

[1] The constitution of this compound is uncertain. If it be $C_6H_2Br_2(OBr)$. COOH, analogy with the body $C_6H_2Br_3.OBr$ would lead one to expect that it would react with potassium iodide to form $C_6H_2Br_2(OH).COOH$, but this implies the combination of $2Br_2$ only, instead of $3Br_2$. On the other hand, the formation of the body $C_6HBr_3(OH).COOH$ is not in accordance with the usual behaviour of ortho-derivatives of benzene, though it accounts for the absorption of $3Br_2$ (see E. Werner, *Bull. Soc. Chim.*, xlvi, 275).

[2] The author has further proved that the change by which the four atoms of bromine at first absorbed is ultimately increased to six occurs gradually, the reaction being accompanied by an evolution of carbon dioxide, but even after many hours the volume of gas does not approach that represented by the above equation. Determinations of the percentage of bromine show that the product obtained is a mixture (Allen and Tankard).

into the reaction.[1] The bottle is closely stoppered, well shaken, and allowed to remain in the dark for at least one hour to ensure the completion of the reaction.[2] Another bottle containing an equal quantity of the bromine solution is similarly diluted and acidified, and left to stand side-by-side with the sample. A solution of potassium iodide (10 per cent.) is next added to the contents of both bottles, and the liberated iodine titrated with a decinormal solution of sodium thiosulphate (24.827 grammes of $Na_2S_2O_3+5H_2O$ per litre). Each 1 c.c. of this thiosulphate solution required represents 0.008 gramme of bromine in excess of that which has reacted with the salicylic acid, 0.138 gramme of which causes the disappearance of 0.480 gramme of free bromine, or as much as will be liberated by about 50 c.c. of the bromine solution. The observation of the end-reaction may be assisted by the use of starch-paste, but it is important that this should not be added until the liquid is nearly decolorised. Hence, if a preparation already containing starch is to be examined, the salicylic acid must first be extracted by alcohol or other suitable solvent, and the process applied to the solution (Fresenius and Grünhut). In the case of wine and beer, the salicylic acid should be first extracted by the use of a mixture of ether and petroleum-spirit, and the process applied to the aqueous liquid obtained on shaking the above solution with caustic soda.

The bromine process of determining salicylic acid is specially valuable in presence of benzoic acid, which is not acted on by bromine in aqueous solution. The precipitate may be filtered off, and the benzoic acid isolated from the filtrate. Cinnamic acid reacts with four atoms of bromine.

A process similar to the above has been described by W. Fresenius and Grünhut (*Analyst*, 1900, p. 19).

COMMERCIAL SALICYLIC ACID.

As now met with in commerce, salicylic acid, though varying much in quality, is free from those gross sophistications which are alleged to have occurred in the past.[3]

[1] This solution is prepared by dissolving 19.5 grammes of bromine (= 6.5 c.c.) in about 100 c.c. of water containing 10 grammes of caustic soda. The liquid thus obtained is boiled well, and then diluted with water to two litres. The solution keeps indefinitely. On addition of hydrochloric acid, the whole of the bromine present is liberated according to the equation:—

$$5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3Br_2 + 3H_2O.$$

[2] A more prolonged standing is desirable when very accurate results are required.

[3] Besides containing more or less sodium chloride, phenol, cresotic acid, and the isomers of salicylic acid as natural impurities, salicylic acid adulterated with potassium sulphate, gypsum, starch, sugar, etc.,

Three distinct qualities of salicylic acid are now recognised in commerce, namely: ordinary acid, which is the cheapest; natural acid, which is the most expensive; and the so-called "physiologically-pure acid," which is intermediate in price. This last variety is a highly-purified synthetical acid, free from any admixture of paracresotic acid. Much of the ordinary salicylic acid of commerce is now of very considerable purity, and is very generally employed in medicine.

The facile formation of definite crystals is a useful indication of the purity of salicylic acid, the presence of foreign matters in its solutions greatly interfering with its crystallisation. Thus the presence of 5 per cent. of paracresotic acid prevents the formation of large crystals, but 2 per cent. produces no material effect.

When agitated with cold concentrated sulphuric acid, salicylic acid should yield a perfectly colourless solution (see page 69).

H. Kolbe gives the following method of testing the purity of salicylic acid:—Dissolve 0.5 gramme of the sample in 5 or 6 c.c. of strong alcohol, pour the clear solution on to a watch-glass, and allow it to evaporate spontaneously. The residual salicylic acid forms a ring of beautifully aggregated efflorescent crystals round the edge of the watch-glass. This mass is pure white if the acid tested be pure and recrystallised, but yellowish or yellow if the simply precipitated acid be used. If the colour be brownish or brown, the sample is unfit for internal use.

Phenol is liable to be present in salicylic acid which has been sublimed. It may be detected by nearly neutralising the sample with sodium carbonate, and agitating the liquid with ether. On gently evaporating the ethereal liquid, the phenol may be recognised by its odour, taste, and chemical reactions.

J. Muter gives the following test for phenol in samples of salicylic acid:—Boil 1 gramme in about 15 c.c. of water, cool, decant the solution, and add to it one drop of a saturated solution of potassium bicarbonate, one drop of aniline, and 5 drops of solution of bleaching-powder, when, if carbolic acid be present, a deep blue colour will be produced. Another test for phenol is to treat 5 c.c. of a saturated aqueous solution of the sample with a crystal of potassium chlorate and 2 c.c. of hydrochloric acid. On pouring ammonia carefully on the surface of the liquid, a reddish or brownish tint will be developed if phenol be present.

According to the British Pharmacopœia (1898), if salicylic acid be shaken up with a small proportion of water, the mixture filtered, and the filtrate evaporated, the residue should be white,

is said to have been met with in America. Mineral adulterants would be left on igniting the sample, and starch and sugar detected by their insolubility in ether.

and have no buff-coloured fringe. The absence of this fringe is stated to prove the absence of iron, colouring matters, and (erroneously) organic impurities.

Para-hydroxybenzoic acid, which is the isomer most likely to be present in commercial salicylic acid, may be partially separated by mixing the hot aqueous solution with excess of milk of lime, when a basic calcium salicylate separates on cooling. A more exact separation may be effected by drying the free acids at 60° C., and agitating with anhydrous chloroform. Salicylic acid dissolves readily, but para- and meta-hydroxybenzoic acids remain largely undissolved.

From benzoic acid, para-hydroxybenzoic acid may be separated by treatment with carbon disulphide, in which the latter acid is nearly insoluble.

While salicylic acid is volatile in a current of steam, the isomeric hydroxybenzoic acids are not volatile, and hence remain in the retort together with hydroxy-isophthalic acid, if present. The last-named compound is now rarely met with in commercial salicylic acid. The cresotic acids behave like salicylic acid (see page 74).

If excess of calcium carbonate be added to a boiling aqueous solution of impure salicylic acid, and the liquid be filtered while hot, sparingly soluble calcium salicylate will be deposited as the solution cools.[1] When re-crystallised and decomposed by hydrochloric acid, this substance yields pure salicylic acid, having identical properties with that obtained from wintergreen oil. If the mother liquor from the calcium salicylate be further concentrated, another crop of impure crystals may be obtained. There remains in solution a very soluble calcium cresotate, which, on decomposition by hydrochloric acid, gives a precipitate of cresotic acid. This, when crystallised from boiling water, forms silvery plates, which are much more soluble than salicylic acid in both hot and cold water. The purification of salicylic acid by this method is very tedious, owing to the numerous recrystallisations necessary.

A useful method of purifying salicylic acid is to convert it into the sodium salt, and subject the solution to fractional precipitation with silver nitrate. The first fractions thrown down consist of pure silver salicylate, from which the free acid can be obtained by treatment with hydrochloric acid. Helbing and Passmore state that paracresotic acid and other impurities are all concentrated in the last fractions of the silver salt, and can thus be readily identified.

[1] If excess of milk of lime be substituted for calcium carbonate, a sparingly soluble basic calcium cresotate is formed, which cannot be separated from the salicylate.

Artificial salicylic acid [1] is very liable to contain one or more of the homologous cresotic acids. For its purification, Dunstan and Bloch recommend that the acid should be treated with lead carbonate, and the resultant lead salts crystallised from dilute alcohol. The lead salicylate is deposited first, and after one recrystallisation, from 70 to 80 per cent. of the original acid can be recovered therefrom in an absolutely pure condition.

Commercial salicylic acid formerly contained a considerable proportion of allied acids. Thus in 1878, J. Williams isolated from 15 to 20 per cent. of these acid impurities, but did not identify them, and Ewell and Prescott found still larger proportions. In 1890, Dunstan and Bloch (*Pharm. Jour.* [3], xxi, 431) further examined the specimens prepared by Williams (which had been preserved in the museum of the Pharmaceutical Society of Great Britain), and showed that they were isomeric modifications of cresotic acid, homologous with salicylic acid (see page 104).

According to M. Charteris, it is to the presence of cresotic acid in artificial salicylic acid that the objectionable symptoms (*e. g.*, delirium, restlessness, etc.) sometimes caused by the latter are attributable, and he states that when the impurity is removed the purified product has therapeutic characters identical with those of the natural acid.[2]

Formerly, commercial salicylic acid was liable to contain all three modifications of cresotic acid, but now a small proportion of the para-cresotic acid only is likely to be present.

The solubility of salicylic acid in boiling water is materially increased by the presence of cresotic acid. If, to a solution of the sample in boiling water, about one-fifth of its volume of alcohol be added and the liquid allowed to cool, pure salicylic acid will form separate, distinct, non-coherent crystals; whereas samples containing a notable proportion of cresotic acid form a network or woolly mass of small or indistinct crystals.

Pure salicylic acid melts sharply between 156° and 157° C., but a very small percentage of para-cresotic acid materially reduces the melting-point of the sample and causes it to

[1] Salicylic acid guaranteed to have been made from oil of wintergreen has been occasionally found to contain appreciable quantities of cresotic acid. This was in some cases due to the fact that the oil of wintergreen from which the acid had been made was nothing more than an artificial oil made in the first instance from artificial salicylic acid, the original impurities of which had been preserved during the various processes.

[2] In 1890, shortly after the first publication of these researches (*Brit. Med. Jour.*, Nov. 30th, 1889), a prosecution under the Sale of Food and Drugs Acts was instituted in Glasgow for selling salicylic acid containing 2½ per cent. of cresotic acid (*Pharm. Jour.* [3], xxi, 394).

soften at a temperature below that requisite to produce actual fusion.[1]

To detect cresotic acid in salicylic acid, B. Fischer (abst. *J. C. S.*, 1890, lviii, 89) recommends the following test:—Calcium carbonate (1 to 2 grammes) is boiled with 15 c.c. of water in a 200 c.c. flask, and 3 grammes of the sample of salicylic acid added. The flask is shaken over a flame till the volume of the contents is reduced to 5 c.c., by which time some crystals will have formed. The liquid is cooled, the crystals separated, and the mother-liquor transferred to a test-tube and evaporated to about 1 c.c. On rubbing the tube containing this concentrated liquid with a glass rod, crystallisation sets in. 1 c.c. of water is then added and the liquid is filtered through a plug of cotton-wool. The filtrate is made up to 1 c.c. and a few drops of hydrochloric acid are added. If the sample contained as much as 3 to 5 per cent. of cresotic acid, a mixture of acids separates which fuses in boiling water and collects in thick oily drops at the bottom of the tube. This test is said to succeed only when the amount of cresotic acid exceeds 1 per cent.

The determination of cresotic acid when in admixture with salicylic acid, if present in sufficiently large proportion, may be effected by careful titration of the sample with caustic soda and phenol-phthaleïn, as recommended by Ewell and Prescott (*Pharm. Record*, 1888; *Analyst*, xiii, 208). B. Fischer (abst. *J. C. S.*, lviii, 88) recommends with reason the replacement of the soda solution by decinormal baryta, which latter solution is necessarily free from carbonate. Fischer points out that the cresotic acid may be seriously over-estimated, unless other impurities—such as moisture, colouring-matter, and sodium chloride—be previously removed. For this purpose he recommends that the sample be dissolved in ether, and the solution filtered from any insoluble matter. The filtrate is then evaporated at a gentle heat, and the residue dried at 60° C., and finally over strong sulphuric acid. When the impurity is simply water it is perhaps preferable to treat the sample with petroleum-ether, agitate the solution with plaster of paris, filter and evaporate to dryness.

In carrying out the operation, about 0.2 gramme of the purified sample, weighed with the greatest possible accuracy, and dried as already described at or below 60° C., is treated with a few

[1] "One can now obtain commercially an acid *physiologically pure*, even the last fraction of which has a melting-point of 156.85° C.; commercial *crystals* with a m. pt. of 156.5° to 156.75°, containing about $\frac{1}{20}$ per cent. impurity, the last 10 per cent. giving a m. pt. $\frac{1}{2}$° C. below the maximum; commercial *powder* with an initial melting-point of 156.4° rising to 156.75° containing $\frac{1}{10}$ per cent. impurity, the last 10 per cent. giving a m. pt. 1° C. below the maximum."—Squire's *Companion to the Pharmacopœia*, 1899.

drops of an alcoholic solution of phenol-phthaleïn, and, without adding water for solution, a centinormal solution of baryta added from a burette, with constant agitation, until the point of neutrality is approached. The flask is then rapidly warmed over a flame while the contents are kept in agitation, avoiding actual boiling until the remainder of the acid is dissolved, when the titration is completed. The baryta is preferably standardised against salicylic acid of known purity.

When pure salicylic acid is treated in the above manner, one gramme requires 726.3 c.c. of centinormal baryta for its neutralisation, whereas an equal weight of one of the modifications of cresotic acid will neutralise only 659.4 c.c. Hence the difference, 66.9 c.c., represents the whole distinction between the two acids, so that the presence of each unit per cent. of cresotic acid will lower the volume of centinormal alkali required for one gramme by 0.669 c.c. Working on 0.2 gramme of the sample, this difference is reduced to 0.134 c.c. Hence extreme care in operating is essential.

Ewell and Prescott (*Pharm. Record*, 1888; *Analyst*, xiii, 237) have proposed a method of determining cresotic acids in admixture with salicylic acid based on their conversion into the corresponding isomers of cresol on distillation with lime. They direct that 15 grammes of the sample of acid and an equal weight of lime should be thoroughly dried and well triturated, together with an equal quantity of dry iron filings, and the mixture heated strongly in a glass retort, the distillate being collected in a well-cooled receiver. The distillate is treated with just sufficient water to liquefy it, and the liquid mixed with an equal measure of caustic soda containing 9 per cent. of NaHO. To this solution cold water is then added gradually until precipitation commences. From the volume of water required to cause precipitation the proportion of cresotic acid present in the sample is found by the following table:—

Volumes of Water Required to Precipitate Mixed Soda and Distillate.	Percentage of Cresol in Distillate.	Percentage of Cresotic Acid in Sample.
6.7	5	4.9
6.0	10	9.8
5.25	15	14.8
4.5	20	19.8
4.0	25	24.7
3.6	30	29.7
3.3	35	34.7
3.1	40	39.7
2.8	45	44.7
2.6	50	49.7

It is evident that such a method as the foregoing can only be roughly approximate, and is useless when the proportion of cresotic acid is very small. In both this case and that of titration with standard alkali it is best to subject a fairly large quantity of the sample to treatment by one of the methods previously mentioned for purifying salicylic acid (by conversion into silver, lead or calcium salt), recovering the acid from the impure fractions, and subjecting it to one of the above methods for the determination of cresotic acid.

B. C. Hesse (*Pharm. Era*, 1889; *Pharm. Jour.* [3], xx, 174) has published a number of interesting suggestions for the determination of impurities in salicylic acid; but the experiments he adduced in support of his proposals were unsatisfactory, or required further verification. Moreover, his methods are mostly applicable only to very large proportions of impurities.

Metallic and Alkaloidal Salicylates.

Salicylic acid possesses the characters both of a phenol and an acid. The hydrogen of the carboxyl group is replaceable by metals, salts of the formula $C_6H_4(OH).COOM$ being formed. The hydrogen of the hydroxyl group (phenolic hydrogen) is also replaceable by alkali-metals, the basic compounds so produced being converted by carbon dioxide into the *monobasic* salicylates. Salicylic acid is monobasic with all indicators of neutrality.

The ordinary or neutral metallic salicylates are well-defined salts, and mostly crystallisable. When heated in the solid state they evolve phenol and carbon dioxide. The residue usually consists of a basic salicylate, but in the case of the potassium compound much para-hydroxybenzoate (p. 63) remains. Secondary products are also liable to be formed.[1]

Solutions of the neutral salicylates give an intense violet coloration with ferric chloride, and respond to the other reactions for salicylic acid (p. 69).

The British Pharmacopœia (1898) states that solutions of sodium salicylate, not more dilute than 1 per cent. strength, give a yellowish-brown precipitate with uranium nitrate solution (distinction from carbolates and sulphocarbolates). With only a small quantity of the uranium nitrate solution, the liquid is coloured brown but no precipitation occurs. Larger quantities of the reagent give the yellow-brown flocculent precipitate of *uranyl salicylate*, which subsequently acquires a "silky" appearance.

On adding dilute sulphuric or hydrochloric acid to a solution

[1] Phenol-sulphonates also evolve phenol when heated, but the residue contains sulphate, at least if sodium nitrate or carbonate be added before ignition.

of a salicylate, salicylic acid is thrown down as a bulky white precipitate, readily dissolving on agitation with ether.

Concentrated solutions of sodium or ammonium salicylate dissolve certain freshly-precipitated metallic hydroxides. Cupric hydroxide dissolves instantaneously in the cold to an emerald-green solution. Ferric and aluminium hydroxides are dissolved by strong solutions of salicylates at 80° C., and chromium hydroxide is soluble with difficulty to a greenish-blue solution. The copper and aluminium solutions obtained in the above manner are not precipitated by sodium or ammonium hydroxide, while the ferric solution is precipitated by caustic soda but not by ammonia. The iron is completely precipitated as sulphide by passing a current of sulphuretted hydrogen through the solution, whereas alumina when present remains in solution. These facts may be utilised for the quantitative separation of small quantities of iron and aluminium. (J. Wolff, *J. S. C. I.*, 1901, p. 1150.)

Sodium Salicylate, $NaC_7H_5O_3$, forms small white crystalline plates or a crystalline powder, odourless and permanent in the air. It has a sweetish, saline and somewhat alkaline taste, and a neutral or feebly acid reaction to litmus. It is soluble in an equal weight of cold water, only slightly soluble in absolute alcohol, but soluble in 8 parts of cold rectified spirit. In boiling water and alcohol sodium salicylate is very soluble. Both the alcoholic and the aqueous solutions give a violet colour with ferric chloride. On ignition, sodium salicylate evolves phenol, and leaves from 30 to 31 per cent. of Na_2CO_3. It is completely soluble in ammonia, and the solution does not reduce silver nitrate, even on boiling. Barium chloride should cause no precipitate in the aqueous solution, and the precipitate with silver nitrate should completely dissolve on addition of nitric acid and alcohol. When the solid salt is shaken in the cold with 15 parts of strong sulphuric acid, no brown coloration should be produced.

As in the case of salicylic acid, three qualities of sodium salicylate are recognised in commerce. Especially if not quite pure, sodium salicylate is liable to become coloured by keeping. This change is more marked when the salt is exposed to air and light. The same is true of the solution, but this may be preserved by the addition of about 1 per cent. of sodium thiosulphate.

Lithium Salicylate, $LiC_7H_5O_3$, forms a white crystalline powder, readily soluble in water and alcohol. As met with in commerce, it usually has an acid reaction. The solubility of this salt in water at 15° is about 1 : 0.8, and in alcohol about 1 : 1.7. Lithium salicylate is employed (in doses of 0.5 to 1.0 gramme) in the treatment of acute or chronic rheumatism.

Ferric Salicylate, $Fe(C_7H_5O_3)_3$, separates, on mixing a strong solution of sodium salicylate with ferric chloride, as a brown precipitate, which, together with the mother-liquor,

rapidly acquires a deep violet colour. After washing, ferric salicylate forms a brown amorphous body, which yields a violet solution on boiling with water.

STRONTIUM SALICYLATE, $Sr(C_7H_5O_3)_2$, forms sparingly soluble crystals. It is highly recommended as an internal antiseptic in place of salol, and in chronic gout and rheumatism, especially when complicated by nervous disorders.

ALUMINIUM SALICYLATE, $Al_2(C_7H_5O_3)_6 + 3H_2O$, is obtained as a precipitate on mixing solutions of an aluminium salt and sodium salicylate. It occurs in commerce under the name of "*Salumen*" as a reddish-white, insoluble powder, which is employed as a dusting powder in catarrhal affections of the nose and pharynx.

Aluminium-Ammonium Salicylate, $Al_2[C_6H_4(ONH_4)CO_2]_6 + 2H_2O$, is a neutral soluble salt which is more stable in solution than in the dry state. Under the name of "*Soluble Salumen*" it is used as an astringent wash for the throat and nasal passages.

Aluminium-Potassium Salicylate has been employed as a combined astringent and antiseptic under the name "*Alkasal*" or "*Alkasol.*" Alkasal is also the name given to an aluminium potassium acetate.

MERCURIC SALICYLATE. A basic compound of the formula $C_6H_4.O.Hg.CO_2$, is obtained by mixing solutions of mercuric nitrate and sodium salicylate, and is now official in the German Pharmacopœia (Edit. iv). It forms a white amorphous powder, insoluble in water and chloroform, but soluble in solution of sodium chloride and other haloid salts. Freshly-prepared mercuric salicylate is more soluble, and gives a stronger ferric chloride reaction than old samples. Mercuric salicylate is also somewhat soluble in ether (1 : 100) and in 95 per cent. alcohol (1 : 45). After keeping for some time, the salt has an acid reaction to litmus. Mercuric salicylate keeps best in solution in sodium chloride. Mercuric salicylate is decomposed by a solution of sodium carbonate.

E. Rupp (abst. *J. S. C. I.*, 1901, p. 604) states that the method given in the German Pharmacopœia for the determination of the mercury in mercuric salicylate (precipitation of mercuric sulphide by sulphuretted hydrogen) is unreliable, and recommends that 0.3 gramme of the salicylate should be rubbed down with a little water and 25 c.c. of decinormal iodine solution run in. After standing for an hour in a well-stoppered flask, the excess of iodine is determined by titration with standard thiosulphate solution. Several determinations required 16.5 to 16.8 c.c. of decinormal iodine, practically no variation being noticed whether the action was allowed to continue for one hour or fifteen. Theoretically, 0.3 gramme of the salicylate should require 17.85 c.c. of decinormal iodine solution. The low results obtained are due to the fact that mercuric salicylate

reacts with haloid salts to form a double compound, but as this is a constant, the results are quite reliable.

BISMUTH SALICYLATE, or, more correctly, *Bismuthyl Salicylate*, $BiO.C_7H_5O_3+H_2O$,[1] is employed to a considerable extent in medicine. It is a white amorphous powder, insoluble in water. The British Pharmacopœia (1898) requires that when the substance is shaken with alcohol of 90 per cent., the filtered liquid shall give no colour with ferric chloride (indicative of free salicylic acid). It is further required that, when precipitated with sulphuretted hydrogen, the salt should yield 70 per cent. (the theoretical quantity is 71 per cent.) of bismuth sulphide, Bi_2S_3. The theoretical quantity of Bi_2O_3 which should be obtained on heating and cautious ignition of bismuth salicylate is 64.3 per cent., but the salt is very liable to yield slightly more oxide. The British Pharmacopœia of 1898 requires from 62 to 64 per cent. of bismuth oxide.[2]

The use of alcohol as a solvent for free salicylic acid in bismuth salicylate is unsatisfactory, since it causes partial decomposition of the latter. W. Lyon (*Pharm. Journ.*, 1904, i, p. 219) prefers to employ 90 per cent. benzol, which is free from this objection.

In the examination of bismuth salicylate the determination of the proportion of bismuth oxide left on ignition will usually be found a sufficient indication of quality, but the salicylic acid may also be separated by acidifying the solution with hydrochloric acid and agitating with ether, when the residue left on evaporation of the ether may be examined for para-cresotic acid.

Although commercial samples of bismuth salicylate may easily be obtained of a fair standard of purity, the percentage of Bi_2O_3 is very variable. From 30 to 75 per cent. of the oxide have been found by various observers.

[1] According to Martinotti and Cornelio (*J. S. C. I.*, 1901, p. 603), commercial bismuth salicylate contains one or both of the following compounds:—

$$C_6H_4(OH).COOBiO; \text{ and } C_6H_4(OH).COOBi(OH)_2.$$

P. Thibault, however (*Chem. News*, 1901, p. 310; *J. S. C. I.*, 1901, pp. 927; 1134), has obtained a true bismuth salicylate, having the formula $Bi_2O_3.(C_7H_6O_3)_3$.

[2] It has been pointed out by several observers that no sample of bismuth salicylate, however carefully prepared, will answer to the official requirements, as the portion extracted by alcohol will invariably give a violet reaction with ferric chloride, while the percentage of bismuth oxide will often reach as much as 66 even in the most carefully prepared specimens. F. B. Power points out that the pharmacopœial requirements are inconsistent, since if less than 64.3 per cent. of bismuth oxide is present there must necessarily be a corresponding excess of salicylic acid, which will give a violet coloration with ferric chloride when shaken out with alcohol.

D. B. Dott (*Pharm. Jour.*, 1895, i, p. 582) has described a sample of so-called bismuth salicylate which contained 47 per cent. of free salicylic acid, as determined by treatment of the sample with ether. Bismuth salicylate is extensively employed for the treatment of gastric catarrh and some intestinal disorders, but the presence of more than insignificant traces of free acid renders the preparation objectionable. Samples having an exceptionally light colour generally contain a notable quantity of free acid.

Commercial bismuth salicylate is very liable to contain small quantities of bismuth *nitrate*, and according to Green and Windridge (*Pharm. Jour.*, 1900, i, 262), this impurity is always present. For its detection, they dissolve the sample in pure sulphuric acid and add the liquid to a solution of brucine in the same acid. This latter often has a pink or rose colour, but in the presence of traces of nitrates the colour becomes a bright red which cannot be mistaken. The reaction with indigo has also been proposed for the detection of nitrate in bismuth salicylate.

I. Kollo (*Proc. Amer. Pharm. Assoc.*, 1899, p. 719) has proposed to assay bismuth salicylate by heating a known weight with excess of normal caustic alkali, filtering off and weighing the resultant BiO.OH (or igniting it to Bi_2O_3), and calculating the salicylic acid from the diminished alkalinity of the filtrate. The results are not very accurate, and any nitrate of bismuth present in the sample will be calculated as salicylate.

F. B. Power has found that Messinger and Vortmann's iodine process (page 74) can be satisfactorily employed for the assay of bismuth salicylate.

Bismuth Cerium Salicylate forms an insoluble pink powder which has proved valuable in the treatment of diseases of the gastric and intestinal mucous membranes.

Sodio-Theobromine Salicylate. A compound of the formula $C_7H_7N_4O_2Na + C_6H_4(OH).COONa$, has received application in medicine under the name of "Diuretin." It is prepared by mixing aqueous solutions of molecular proportions of sodium salicylate and sodium-theobromine, and evaporating to dryness. Diuretin is a white amorphous powder, freely soluble in water, but decomposed by acids. It is employed as a diuretic in cases of scarlet fever, nephritis, etc. (dose: adults, 20 to 40 grains; children, 8 to 24 grains). "*Uropherin*" is the lithium compound corresponding to diuretin. It is recommended as a diuretic in doses of 15 grains.

ANTIPYRINE SALICYLATE is known commercially as "*Salipyrin.*" It is an odourless crystalline powder melting at about 91°. It has a pleasant taste, and possesses the properties of its constituents. *Tolypyrine salicylate*, commercially known as "*Tolysal,*" melts at 101°, and closely resembles salipyrin.

QUININE SALICYLATE is used to a considerable extent as an antipyretic in typhus, and as a remedy for gout and rheumatism. It forms fine white needles of the formula $C_{20}H_{24}N_2O_2,C_7H_6O_3+H_2O$. It should contain 70 per cent. of quinine, but is very liable to be contaminated with excess of salicylic acid, for which impurity it should always be examined. Quinine salicylate dissolves in about 1000 parts of cold or 230 parts of boiling water, in 24 parts of 90 per cent. alcohol, and in 25 parts of chloroform.

"*Saloquinine*," $C_6H_4(OH).COO.C_{20}H_{23}N_2O$, the quinine-ester of salicylic acid, has been recommended as an analgesic; and "*Rheumatine*," the salicylate of saloquinine, is said to be of value in rheumatic affections.

COLCHICINE SALICYLATE, known in commerce as "*Colchisal*," is used, in doses of one-hundredth of a grain, in the treatment of arthritis, gout, and rheumatism. It forms a yellow amorphous powder, soluble in water, alcohol and ether. The name "colchisal" is also applied to a mixture of colchicine and methyl salicylate. The preparation is dangerous in cases of kidney disease.

SALICYLIC ESTERS.

Several of the esters of salicylic acid are of considerable commercial importance, and this is specially the case with the methyl and phenyl esters.

METHYL SALICYLATE. $C_6H_4(OH).COO(CH_3)$. This compound occurs naturally in the leaves of the *Wintergreen* (*Gaultheria procumbens*) and the bark of the *Sweet Birch* (*Betula lenta*), and the essential oils from these sources consist of methyl salicylate in an approximately pure condition. Methyl salicylate occurs in smaller proportion in various other plants,[1] but usually in the form of the crystallisable glucoside *gaultherin*, which under the influence of the soluble ferment *betulase* splits up into dextrose and methyl salicylate:—$C_{14}H_{18}O_8+H_2O=C_6H_{12}O_6+C_6H_4(OH).COO(CH_3)$. The ester of wintergreen leaves and betula bark exists chiefly in the form of the glucoside, but in the former case some ready-formed methyl salicylate is also present.

[1] In addition to the sources mentioned in the text, methyl salicylate or its glucoside has been found to occur in plants of many different orders (see *Schimmel & Co.'s Reports*, April, 1898; October, 1899; April, 1900). Van Romburgh found it in 160 out of 900 plants examined by him; but in all cases the fresh leaves gave no indication of the ester, the presence of which was detected when leaves which had been kept some days were distilled, a fact which favours the view that the ester exists naturally as a glucoside or similar complex form.

Salicylic acid exists, probably as methyl salicylate, in minute proportions (0.0005 to 0.002 gramme per kilogramme) in various fruits, including strawberries, raspberries, blackberries, mulberries, plums, cherries, apples, oranges, grapes, and consequently in wine (*J. S. C. I.*, 1902, xxi, 1416; *J. Amer. Chem. Soc.*, xxv, 242).

In addition to the foregoing natural sources, methyl salicylate is now manufactured synthetically on a considerable scale, by distilling two parts of salicylic acid with two of methyl alcohol and one of strong sulphuric acid. An alternative process, which is said to give good results, is to pass dry hydrochloric acid gas through a saturated solution of salicylic acid in methyl alcohol (H. T. Thayer, *Amer. Jour. Pharm.*, lxvii, 243; *Pharm. Jour.* [3], xxv, 1090).

Pure methyl salicylate is a colourless or yellowish oil of peculiar aromatic odour. It has a specific gravity of 1.1819 at 16°, and boils under the ordinary atmospheric pressure at 224°. If shaken with water and the aqueous liquid then treated with ferric chloride a deep violet coloration is produced. When boiled with caustic alkalies methyl salicylate is hydrolysed with formation of methyl alcohol and a salicylate, but with cold, dilute caustic potash solution it reacts to form a crystalline compound of the formula $C_6H_4(OK).COOMe$.

Methyl salicylate is now manufactured in a state of considerable purity, and is extensively used in the treatment of rheumatism and kindred affections. It is known in commerce as "artificial wintergreen or gaultheria oil," and is said to be preferable to the natural oils of wintergreen and sweet birch, as being less liable to adulteration.[1]

Natural Gaultheria or *Wintergreen Oil* (from *Gaultheria procumbens*) contains about 99 per cent. of methyl salicylate (Power and Kleber).[2] The remaining 1 per cent. was isolated by repeatedly shaking an ethereal solution of the oil with caustic potash solution, as described under birch oil (p. 89). Only 1.05 per cent. of the sample survived this treatment, and on evaporation of ether was obtained as a mass which was semi-solid at the ordinary temperature. Power and Kleber isolated from it the following bodies:—A *paraffin*, melting at 65.5°, and of the probable formula $C_{30}H_{62}$; an *aldehyde* or *ketone*, which when separated in a pure form from its bisulphite compound had an odour like that of œnanthic aldehyde; a secondary *alcohol*, $C_8H_{16}O$, boiling between 160° and 165° and corresponding to the above aldehyde or ketone; and an *ester* which on saponification yielded the above alcohol and an acid containing $C_6H_{10}O_2$,

[1] In large quantities, methyl salicylate has marked toxic properties. A fatal case of poisoning of a middle-aged farmer who took two ounces of wintergreen oil in mistake for whisky has been recorded by B. Pillsbury (*New York Med. Record*, lviii, 150). Death occurred from exhaustion in forty-one hours.

[2] Cahours, in 1844, found wintergreen oil to contain 90 per cent. of methyl salicylate and 10 per cent. of a terpene boiling at 160°, which he called "gaultherilene." Recent analyses of gaultheria oil have failed to confirm this observation and it is highly probable that the oil examined by Cahours was adulterated with turpentine oil.

resulting by oxidation from the ketone.[1] The alcohol and ester possessed the penetrating characteristic odour which distinguishes wintergreen oil from artificial methyl salicylate, and gives the natural product its special value as a perfume.

True gaultheria oil is a colourless, yellow, or reddish liquid of a characteristic, strongly aromatic odour, which is different from that of birch oil or artificial methyl salicylate. The specific gravity of the natural oil ranges from 1.175 to 1.187, and the boiling-point from 218° to 221° C. The oil is readily soluble in alcohol, ether, chloroform, and glacial acetic acid.

True gaultheria oil (now commercially almost obsolete) differs from birch oil and artificial methyl salicylate in being feebly optically active, the value of $[\alpha]_D$ being —0.45° to —1°. This character is the only one besides the odour by which gaultheria oil is distinguishable from sweet birch oil, which is now very generally substituted for it.

Oil of Sweet Birch is prepared from the bark of *Betula lenta*, a tree growing extensively in some of the older of the United States.[2] It is colourless or yellowish, but sometimes has a reddish tint from the presence of traces of iron. In odour and taste birch oil is practically indistinguishable from pure methyl salicylate, in both of which respects it differs from wintergreen oil. The optical neutrality of birch oil also distinguishes it from wintergreen oil, but the specific gravity and boiling-point are identical for the two oils.

According to Power and Kleber (1895), sweet birch oil is composed almost wholly of methyl salicylate, of which it contains 99.8 per cent. To separate the small proportion of other constituents, Power and Kleber dissolve the oil in ether, and shake with a 7½ per cent. solution of caustic potash in water, when potassium methyl salicylate passes into the aqueous liquid and the other constituents are retained by the ether. By evaporation of the separated ether Power and Kleber obtained a residue from which they isolated a paraffin and ester apparently identical with those found by them in gaultheria oil; but the secondary alcohol accompanying these compounds was not found in birch oil. Both the natural and artificial varieties of methyl salicylate resemble salicylic acid in giving a deep violet coloration when their alcoholic or aqueous solutions are treated with ferric chloride.

The commercial forms of methyl salicylate, especially those of so-called natural origin, are liable to adulteration with alcohol,

[1] Trimble and Schröter found wintergreen and birch oils to contain traces of alcohol and benzoic acid.

[2] On the Production and Purification of Oil of Birch see the *Scientific American*, June 13th, 1891; *Amer. Journ. Pharm.*, Dec., 1891; *Pharm. Jour.*, 1892, xxii, 4, 593.

chloroform, sassafras oil, oil of camphor, and petroleum. The specific gravity of the sample affords a good indication of sophistication, since all the above-named adulterants except chloroform are of less density than methyl salicylate. The solubility of the oil in 70 per cent. alcohol is also decreased by the presence of most adulterants.

If either of the forms of methyl salicylate be treated in a graduated tube with ten volumes of a 5 per cent. aqueous solution of caustic potash, it dissolves entirely, either at once or on placing the tube in boiling water, whereas any admixed oils remain undissolved, and if present in sufficient proportion can be measured. As the odour of the methyl salicylate is entirely destroyed by the treatment with alkali, the presence of chloroform and other adulterants of strong odour becomes apparent at this stage. The residual odour also distinguishes true gaultheria oil from oil of sweet birch or artificial methyl salicylate.

Chloroform may also be detected by the smell when the oil is warmed. Samples containing chloroform have a high density and low boiling-point, while the density is diminished by the presence of *alcohol*. The chloroform may be approximately separated and determined by fractional distillation, or by estimating the hydrochloric acid formed on passing the vapour mixed with hydrogen through a red-hot tube. In the portion from which the alcohol and chloroform have been separated by distillation, oil of sassafras may be recognised by its odour after addition of a hot concentrated solution of caustic potash. *Sassafras oil* may also be detected by adding 3 or 4 drops of nitric acid (of 1.3 to 1.4 sp. gr.) to 4 or 5 drops of the oil. Sassafras oil becomes blood-red in colour, and soon changes to a brown or dark red amorphous mass. Pure methyl salicylate is unchanged at first, but after some hours it solidifies to a mass of colourless crystals, consisting of methyl nitrosalicylic acid.

The presence of *petroleum* greatly modifies the solubility of methyl salicylate in alcohol, besides reducing the specific gravity. *Oil of camphor* will be rectified before being used as an adulterant. If the lighter fractions be employed these will reduce the specific gravity of the sample and render it optically active; and the terpenes of the camphor oil can be distilled off and further examined. The heavier fractions of camphor oil contain much safrol, which can be recognised by its odour after the methyl salicylate has been saponified.

A useful control on the foregoing tests is obtained by actual determination of the real methyl salicylate present. This may be effected by saponifying the oil with a known quantity of caustic alkali, and determining the excess by titration with standard acid and phenolphthaleïn, as in Koettstorfer's method for oils; by acidulating the liquid after saponification, extracting

the liberated salicylic acid with ether, and titrating the separated ethereal solution; or by treating the sample with alkali and standard iodine, and titrating the acidulated liquid with standard thiosulphite, as practised by Messinger and Vortmann. Although the oils from *Gaultheria procumbens* and *Betula lenta* contain other esters which are expressed in terms of methyl salicylate when the saponification method of assay is employed, Schimmel & Co. prefer that process to the iodine method.

Schneegans and Gerock (*Pharm. Centralb.*, xxxiii, 40) recommend the following as a satisfactory method of detecting free salicylic acid in such substances as artificial oil of wintergreen. One volume of the oil is shaken with 500 volumes of water, and to 100 c.c. of the liquid is added 1 c.c. of a very dilute solution of ferric chloride. If, on the addition of 5 c.c. of chloroform, the violet colour formed disappears, free salicylic acid is absent; but if it persists, the acid is present. This reaction is said to be reliable to the extent of 0.02 milligramme in 1 gramme of the oil.

ETHYL SALICYLATE, $C_6H_4(OH)C.OO(C_2H_5)$, has an odour and other characters very similar to the methyl ester. It is of no commercial interest.

BENZYL SALICYLATE, $C_6H_4(OH).COO(C_7H_7)$, is obtained by heating benzyl chloride with a metallic salicylate to 130°–140°. It is a liquid without odour, boiling at 208° C., and has been suggested as an external remedy.

PHENYL SALICYLATE. SALOL. $C_6H_4(OH).CO.O.C_6H_5$. This body is now manufactured by heating the product of the action of carbon dioxide on sodium phenate with phosphorus oxychloride or pentachloride, when phenyl salicylate and metaphosphate and sodium chloride result. Phosgene (carbonyl chloride) may be substituted for phosphorus pentachloride (*Jour. Soc. Chem. Ind.*, 1886, v. 677).

Phenyl salicylate crystallises in rhombic prisms which melt at 42° to 43° C. It usually occurs as a white crystalline powder of very faint aromatic odour, but the dilute alcoholic solution has a smell resembling that of wintergreen oil, probably owing to the formation of traces of ethyl salicylate. It is almost tasteless, and nearly insoluble in water, but dissolves in alcohol, ether, chloroform, petroleum-spirit, and liquefied carbolic acid.

The alcoholic solution of salol is coloured violet by ferric chloride, while bromine gives a precipitate in the form of long needles, consisting of a bromo derivative,[1] crystallising from alcohol in silky needles which melt at 98°.5 C. When boiled with caustic soda, salol is readily saponified, and the solution

[1] The formula of this derivative is given by some authorities as $C_{13}H_9O_3Br$, but seeing that salicylic acid and phenol are both converted by excess of bromine into the compound $C_6H_2OBr_4$, the alleged composition appears highly improbable.

when acidulated with hydrochloric acid gives an odour of phenol and a copious precipitate of salicylic acid, which after filtration and washing with cold water gives with hot water a solution rendered violet by ferric chloride.

Salol should not redden moistened litmus-paper; and when shaken with 50 parts of water should yield a filtrate which is not rendered violet on addition of one drop of ferric chloride, nor give any immediate turbidity on adding silver nitrate or barium chloride.

Salol is employed in medicine as a substitute for metallic salicylates and wintergreen oil. Being insoluble, it passes unchanged through the stomach, but in the duodenum is decomposed into phenol and salicylic acid, and these products can be detected in the urine, which is usually very dark in colour. As an antipyretic, antiseptic, and antirheumatic, salol possesses properties of value. When applied externally it has no corrosive action, and its lower melting-point gives it some advantages over salicylic acid.

Salol is sometimes employed in skin and nasal diseases as a substitute for iodoform. When melted with camphor (65 : 84) it forms a permanent liquid, suitable for this purpose.

A 5 per cent. solution of salol in weak alcohol, flavoured in various ways, is employed for mouth washes, dentifrices, toilet-powders, etc.

Chlorsalol, or *Chlorophenyl Salicylate*, $C_6H_4(OH).COO(C_6H_4Cl)$, exists in two modifications. *Ortho*-chlorophenyl salicylate forms colourless crystals melting at 85° and has been used in surgery as an antiseptic. The *para*-modification melts at 72°, is insoluble in water but soluble in alcohol, and in doses of 4 to 6 grammes daily has been used internally as a substitute for salol.

A body analogous to salol may be obtained by substituting resorcinol for phenol. By heating a mixture of sodium salicylate and cresylate with phosphorus oxychloride, the salicylate corresponding to ortho-, meta-, or para-cresol is obtained according to the modification of cresol employed. The products are termed "*Cresalols*," and have been employed as dusting powders and substitutes for salol.

Alphol and *Betol* (or *Salinaphthol*) are the commercial names of compounds obtained by the action of sodium salicylate on α- and β-naphthol respectively, in the presence of phosphorus oxychloride. Betol, which is the preferable isomer, is used as an intestinal antiseptic in cases of ague and articular rheumatism. It is tasteless and odourless, with a melting-point of 95°. It is almost insoluble in water, but dissolves readily in alcohol and ether.

Anhydrides of Salicylic Acid.

SALICYLIC ANHYDRIDE, or DI-SALICYLIC ACID,

$$[C_6H_4(HO).CO]_2O,$$

results from the action of phosphorus oxychloride on sodium salicylate, and is also formed by the prolonged heating of salicylic acid with acetyl chloride. It is amorphous, soluble without decomposition in cold sodium carbonate solution, but converted into salicylic acid by boiling with caustic alkalies. It gives a violet coloration with ferric chloride.

SALICYLIDE; TETRASALICYLIDE, $\left\{ \begin{matrix} O.C_6H_4.CO_2.C_6H_4CO \\ CO.C_6H_4O.CO.C_6H_4O \end{matrix} \right\}$ This body, melting at 260°, is formed, together with a polymer, melting about 325°, when a solution of salicylic acid in xylene is treated with phosphorus oxychloride. The two compounds are separated by boiling chloroform, with which the salicylide forms a compound of the formula $(C_7H_4O_2)_4,2CHCl_3$, which crystallises in fine quadratic octahedra containing 33 per cent. of loosely-combined chloroform. It has been utilised for the preparation of pure chloroform (Anschütz, *Annalen*, cclxxiii, 94). A similar compound can be obtained from orthocresotic acid.

Disalicylide, $(C_6H_4CO_2)_2$, has been described by Einhorn and Pfeiffer (*Ber.*, 1901, xxxiv, 2951).

Hydroxy-Benzaldehydes. $C_7H_6O_2$.

ORTHO-HYDROXY-BENZALDEHYDE, $C_6H_4(OH)^1.(COH)^2$, originally known as *salicylous* or *spiroylous acid*, is the aldehyde of salicylic acid, to which it bears the same relation as ordinary aldehyde does to acetic acid. It occurs in the essential oils of the different varieties of *Spiræa*, and likewise in the oil of *Crepis fœtida*. Salicylic aldehyde is also obtained by the oxidation of its alcohol, *saligenol*,[1] or of those glucosides which yield that body on hydrolysis, such as saligenin and populin. It is most readily obtained by warming 20 parts of sodium hydroxide, 10 parts of phenol, and 30 parts of water to about 50°, and then gradually adding 15 parts of chloroform. After warming the mixture for half an hour, it is acidified, when the salicylic aldehyde separates:—$C_6H_5OH + 3NaOH + CHCl_3 = C_7H_6O_2 + 3NaCl + 2H_2O$.

For the preparation of salicylic aldehyde from salicin, 3 parts of the latter body should be warmed with a mixture of 3 parts

[1] SALIGENOL, saligenin, or ortho-hydroxy-benzyl alcohol, $C_6H_4(OH).CH_2OH$, is described at length under "Salicin," Vol. III, Part iii.

of potassium bichromate and 4.5 parts of sulphuric acid with 36 parts of water. The product is steam-distilled, the distillate extracted with ether, and the ether evaporated. The residue of salicylic aldehyde is finally purified by conversion into its sodium bisulphite compound in the usual manner.

When prepared synthetically, salicylic aldehyde is usually contaminated with the corresponding *para*-aldehyde, from which, however, it is easily separated by distillation in a current of steam, in which the *ortho*-compound is easily volatile, whereas the *para*-body is not.

Salicylic aldehyde is a colourless oily liquid, of pleasant aromatic odour, resembling that of oil of meadowsweet (*Spiræa ulmaria*). It has a specific gravity of 1.1731 at 13.5°, and boils at 196.5°. It is fairly soluble in water, easily so in alcohol and ether, and is readily extracted from its aqueous solutions by the last-named solvent. Salicylic aldehyde combines with bisulphites of the alkali-metals to form crystalline compounds, decomposed by dilute acids with the re-formation of the aldehyde. On oxidation salicylic aldehyde yields salicylic acid, and like the latter body, its aqueous solutions yield a deep violet colour with ferric chloride. Like all *ortho*-hydroxy-aldehydes, it colours the skin a deep yellow. Its acid characters are so pronounced that it dissolves in solutions of caustic alkalies to form crystalline compounds, and even decomposes carbonates. In doses of 0.1 to 0.5 gramme, salicylic aldehyde has been employed as an internal antiseptic and diuretic.

PARA-HYDROXY-BENZALDEHYDE, $C_6H_4(OH)^1.(COH)^4$, is isomeric with salicylic aldehyde. Its methyl ether is the well-known *anise aldehyde*, or *para*-methoxy-benzaldehyde, $(CH_3O)^1.C_6H_4.(COH)^4$, which is known in commerce as "*aubèpine*" or "artificial hawthorn." It forms the basis of many perfumes, especially of that known as "new-mown hay." It results from the oxidation of several essential oils, such as aniseed and fennel, which contain anethol (see page 358), and exists therein in greater or less quantity according to the age of the oils. Anise aldehyde can also be prepared synthetically. It is an aromatic oil of specific gravity 1.123 at 15°, and boils at 248°. On oxidation it yields *anisic acid* (page 101).

Derivatives of Salicylic Acid.

In addition to its salts, esters, etc., already described, the following derivatives of salicylic acid are of practical interest. Their chief applications are as antiseptics and anti-rheumatics.

DERIVATIVES OF SALICYLIC ACID.

Chemical Nature.	Formula.	Commercial Name.	Melting-point, °C.	Solubility in: Water.	Solubility in: Alcohol.	Solubility in: Ether.	Coloration with Ferric Chloride.	Therapeutic Applications.	Dose.
Di-iodo-salicylic acid	$C_6H_2I_2(OH) . COOH$	..	220 to 230	Sparingly.	Readily.	Readily.	..	Analgesic, antithermic, and antiseptic.	1.5 to 4.0 grammes.
Sodium Di-iodo-salicylate	$C_7H_3O_3I_2Na + 5H_2O$	..	..	1 : 50	..	..	..		0.5 to 1.0 gramme.
Methyl-Di-iodo-salicylate	$C_7H_3O_3I_2. CH_3$	Sanoform.	110	..	Hot, 1 : 10.	Sol.	..	Desiccant for wounds and ulcers. Substitute for iodoform.	External use.
Di-thio-salicylic acid (No. 1 and No. 2)..	$(C_7H_5O_3)_2 . S_2$	..	..	..	..	..	..	Substitutes for iodoform.	External use.
Sodium Di-thio-salicylate (No. 1)....	$(C_7H_4O_3Na)_2S_2$	Dithion.	..	Sol.	..	..	..	Antiseptic; remedy for foot-and-mouth disease.	External use.
Sodium Di-thio-salicylate (No. 2)....			..	Hygroscopic.	..	..	..	Antiseptic; remedy for muscular rheumatism and rheumatic fever.	0.2 to 1.0 gramme.

Derivatives of Salicylic Acid.—(*Continued.*)

Chemical Nature.	Formula.	Commercial Name.	Melting-point, °C.	Solubility in: Water.	Solubility in: Alcohol.	Solubility in: Ether.	Coloration with Ferric Chloride.	Therapeutic Applications.	Dose.
Basic Bismuth Dithio-salicylate	..	*Thioform.*	..	Insol.	..	..	..	In diseases of eye, ear, *nose and* throat; and in *veterinary medicine* as substitute *for iodoform* in treatment of *eczema*, erysipelas, etc.	External use.
Salicyl-sulphonic acid	$C_6H_3 . (SO_3H) . (OH) . COOH$	Sulpho-salicylic acid.	120	Readily.	Sol.	..	Violet.	In articular rheu*matism*; valuable reagent for *proteids.*	..
Sodium sulpho-salicylate	$C_6H_3 . (SO_3Na) . (OH) . COOH$	..	..	Readily.	Insol.	Insol.	..	*Internal* antiseptic; substitute *for salol.*	..
Ortho-Amido-salicylic acid.........	$C_7H_5O_3 . (NH_2)$	..	..	Cold, insol.; hot, sparingly.	Insol.	Insol.	Cherry-red colour to brown-black ppt.	In articular *rheumatism.*	0.25 to 0.5 gramme.
Methyl-*p*-amido-*m*-hydroxy-benzoate.	$C_7H_4O_3(NH_2) . (CH_3)$	Orthoform.	120	Sparingly.	..	..	Brown.	*Antiseptic* and local anæsthetic.	External use and internally, 0.5 to 1.0 gramme.

Sodium salt of methyl-*p*-amido-*m*-hydroxy-benzo-sulphonate	$C_7H_3O_3(SO_3Na).(NH_2).(CH_3) + H_2O$	Sulphonated Orthoform.	269	Readily.	..	..	..	Substitute for orthoform.	..
Methyl-*m*-amido-p-hydroxy-benzoate	$C_7H_4O_3.(NH_2).(CH_3)$	New Orthoform.	142	Somewhat sol.	..	..	Green colour and dirty green ppt.	Substitute for orthoform.	..
Acetyl-salicylic acid	$C_6H_4.(O.C_2H_3O).COOH$	Aspirin.	135	Insol.	Sol. (1:15)	..	Intense violet.	Anti-rheumatic; substitute for salicylates.	..
Acet-amido-ethyl salicylic acid	$C_6H_3.(O.C_2H_5)(NH.CO.CH_3)COOH$	Benzacetin.	205	Insol.	..	..	..	Anti-neuralgic.	0.5 to 1.0 gramme.
Acetyl-*p*-amido-phenyl salicylate	$C_6H_4(OH).CO_2.C_6H_4[NH(COCH_3)p]$	Salophen.	187 to 188	Insol.	Sol.	Sol.	Violet.	Substitutes for salol; in rheumatism, neuralgia and influenza.	1 to 2 grammes.
Acetonyl salicylate	$C_6H_4(OH).CO_2.(CH_2.CO.CH_3)$	Salacetol; Salantol.	71	Almost insol.	Cold, slightly, hot, readily.	Hot, readily.	..		2 to 3 grammes.
Condensation product of salicylic and gallic acids	$C_6H_4(OH).CO.O.CO.C_6H_2.(OH)_3$	Salitannol.	210	Insol.	Sparingly.	Insol.	..	Antiseptic; substitute for salol.	Chiefly external use.
Condensation product of boric and salicylic acids	$B.OH.(O.C_6H_4.COOH)_2$	Boro-salicylic acid.	..	..	..	..	..	Antiseptic.	External use.
Mixture of boric acid and sodium salicylate		Borsalyl; Borosalyl.	..	Sol.	..	..	..	Antiseptic.	External use.
Salicylamide	$C_6H_4.(OH).CO.(NH_2)$	..	138	1 : 250	Sol.	Sol.	..	Substitute for salicylates.	0.1 to 0.3 gramme.
Salicyl-α-methyl-phenylhydrazone	$C_6H_5.(CH_3).N.N:CH.(C_6H_4).OH$	Agathin; Cosmin.	74	Insol.	Sol.	Sol.	..	Anti-neuralgic and anti-rheumatic.	0.12 to 0.5 gramme.

SALICYL-SULPHONIC ACID. $C_6H_3(SO_3H)(OH).COOH$. This compound, sometimes termed sulpho-salicylic acid, is prepared by heating salicylic acid with twice its weight of sulphuric anhydride at 100°, until dissolved. On cooling and standing, brownish crystals of the sulphonic acid separate, and may be purified by crystallisation from boiling water.

Sulphosalicylic acid forms long, thin needles, which melt at 120° and are very soluble in water. They are coloured a deep reddish-violet by ferric chloride. On fusing sulphosalicylic acid with caustic potash, phenol and salicylic acid are produced, without any dihydroxybenzene being formed.

Sulphosalicylic acid is a delicate reagent for albumin and is a useful precipitant of all varieties of proteids in urine.[1]

Sodium Sulphosalicylate, $C_6H_3(OH).(COOH).SO_3Na$, is obtained by partially neutralising sulphosalicylic acid with sodium carbonate, so as to saturate the sulphonic group only. It is a readily soluble salt, which has found application as an internal antiseptic. It is stated to possess all the advantages of salol, without having the tendency of the latter to liberate free phenol in the system.

Homologues of Salicylic Acid.

A large number of acids are known of the empirical formula $C_8H_8O_3$. Thus:—

(A.) Phenyl-glycollic Acids. Mandelic Acid..$C_6H_5.CH\begin{cases}COOH\\OH\end{cases}$

(B.) Hydroxy-methyl-benzoic Acids........$C_6H_4\begin{cases}COOH\\CH_2.OH\end{cases}$

(C.) Methoxy-benzoic Acids (*e.g.*, Anisic Acid) $C_6H_4\begin{cases}COOH\\O.CH_3\end{cases}$

(D.) Hydroxy-phenylacetic Acids..........$C_6H_4\begin{cases}CH_2.COOH\\OH\end{cases}$

(E.) Hydroxy-toluic Acids (*e. g.*, Cresotic Acids) ....$C_6H_3(CH_3)\begin{cases}COOH\\OH\end{cases}$

Ten chemical modifications of hydroxy-toluic acid exist, and three each (ortho-, meta-, and para-) of hydroxy-phenylacetic, methoxy-benzoic and hydroxy-methylbenzoic acids are known.

[1] A few crystals of the reagent should be added to a small quantity of the clear urine and the liquid agitated, when a turbidity or actual precipitate will be formed if a proteid be present. The precipitate produced by albumins and globulins is not affected by heat, whereas that due to albumoses and peptones dissolves, reappearing as the liquid cools. No normal or abnormal constituent of urine other than proteids is precipitated by the reagent, but these are very completely separated. One part of egg albumin in 20,000 of water can be detected by the test (Roch, *Pharm. Centr.*, 1889, p. 549).

The hydroxy-phenylacetic acids are analogues of hydracrylic acid, while mandelic acid corresponds to ordinary lactic acid.

The hydroxy-methylbenzoic acids are alcohols, whereas the hydroxy-phenylacetic and hydroxytoluic acids have a phenolic constitution.

MANDELIC ACID, $C_6H_5.CH(OH).COOH$, contains an asymmetric carbon atom, and hence, like lactic acid, occurs in three physical isomeric forms, two of which exhibit optical activity in opposite directions ($[\alpha]_D = 158°$ at 20° C.), while the third or racemoid variety is obtainable by mixing the two optically active isomerides in equal proportions.

Inactive or *racemic mandelic acid* may be prepared by boiling together, for thirty-six hours, benzaldehyde, hydrochloric acid, and excess of hydrocyanic acid. *Mandelo-nitrile*, a compound existing in bitter-almond oil, is first formed, and this is hydrolysed by the hydrochloric acid with formation of mandelic acid and ammonia:—

$$\underset{\text{Mandelo-nitrile.}}{C_6H_5.CH(OH).CN} + 2H_2O = \underset{\text{Mandelic Acid.}}{C_6H_5.CH(OH).COOH} + NH_3.$$

The product is shaken with ether, and the acid left on evaporation of the ether re-crystallised from water.

Inactive mandelic acid may also be obtained by other synthetical reactions. It crystallises in trimetric prisms, melts at 118°, and is readily soluble (16 : 100) in cold water, alcohol, and ether. On oxidation by nitric acid, mandelic acid first yields *benzoylformic* and ultimately *benzoic acid*.

The *optically-active mandelic acids* behave like the inactive acid with reagents, but melt at 133°. The lævo-rotatory modification occurs naturally, and may be obtained by digesting amygdalin with fuming hydrochloric acid for some hours at 100°. Fermentation of the ammonium salt of the inactive acid with *Penicillium glaucum* destroys the lævo-acid and leaves the dextro-modification; whereas *schizomycetes* destroy the dextro-acid and leave the lævo-rotatory modification. The two active modifications can be prepared from the inactive acid by converting it into a cinchonine salt and adding a crystal of cinchonine dextro-mandelate, when the salt of the dextro-acid crystallises out, leaving that of the lævo-acid in solution.

HYDROXYMETHYL-BENZOIC ACIDS. $C_6H_4(CH_2OH).COOH$. The ortho-modification melts at 120° (with simultaneous conversion into the anhydride, "phthalide"), the meta- at 180°, and the para-acid at 181°.

Ortho-hydroxymethyl-benzoic acid is obtained by the action of alkalies on its anhydride, *phthalide*. On acidifying the solution the acid is precipitated as a powder slightly soluble in cold water but readily in alcohol. When heated to its melting-point, the

acid is converted into its anhydride, which is also formed by simply boiling the acid with water.

Ortho-hydroxymethyl-benzoic Anhydride, or *Phthalide*, C_6H_4:$(CO.^{(1)}CH_2^{(2)})O$. This compound is formed as stated above, and may be obtained by a variety of synthetic reactions. It crystallises from boiling water in needles which have an odour like that of cinnamon. Phthalide melts at 73° and boils at 295°.[1] It does not combine with acid sulphites nor reduce ammonio-silver nitrate, and it yields no compound with hydroxylamine. Phthalide is oxidised to phthalic acid by treatment with alkaline permanganate. It is reduced to ortho-toluic acid by heating with hydriodic acid and phosphorus, and yields ortho-toluic acid with a little ortho-xylene when heated with zinc dust.[2]

METHOXYBENZOIC ACIDS. $C_6H_4(OCH_3).COOH$. The three modifications of this compound have the following characters:—

	COOH : OCH₃.	M. PT. °C.	B. PT. °C.	CRYSTALLINE FORM.
Ortho-acid. Methyl-salicylic acid	1 : 2	98.5°	...	Monoclinic tablets and prisms.
Meta-acid.........	1 : 3	107°	...	White needles.
Para-acid. Anisic acid	1 : 4	185°	280°	Monoclinic prisms or needles.

Ortho-methoxybenzoic Acid or *Methyl-salicylic acid* is isomeric with methyl salicylate (p. 87).[3] It crystallises from hot water

[1] According to Richter (*Organic Chemistry*), phthalide melts at 83° and boils at 290° C.

[2] MECONIN, which occurs ready-formed in opium, has the constitution of a *dimethoxy-phthalide*. It is the anhydride of *meconinic acid*, which is only known in its salts, though the corresponding aldehydic acid, *opianic acid*, is well known as a product of the oxidation of narcotine. The following formulæ show the relationship of these bodies:—

Hydroxymethyl-benzoic Acid, ... $C_6H_4\begin{cases}COOH\\CH_2OH\end{cases}$	Phthalide, $C_6H_4\left\{\begin{matrix}CO\\CH_2\end{matrix}\right\}O$
Meconinic Acid, $.C_6H_2(CH_3O)_2\begin{cases}COOH\\CH_2OH\end{cases}$	Meconin, $C_6H_2(CH_3O)_2\left\{\begin{matrix}CO\\CH_2\end{matrix}\right\}O$
Opianic Acid, ... $C_6H_2(CH_3O)_2\begin{cases}COOH\\COH\end{cases}$	

[3] When methyl salicylate is heated to 100°–120° with caustic potash and excess of methyl iodide, it is converted into the methyl ester of ortho-methoxybenzoic acid, $C_6H_4(OCH_3).CO.OCH_3$, which is a liquid boiling at about 245°. The mixture is freed from methyl alcohol and methyl

in large monoclinic tablets, and from alcohol in prisms, melting at 98.5°, and decomposing above 200° into *anisol*, $C_6H_4.OCH_3$, and carbon dioxide. When heated with concentrated hydrochloric or hydriodic acid, methyl-salicylic acid yields salicylic acid and methyl chloride or iodide.

Methyl-salicylic acid gives no violet coloration with ferric chloride.

Anisic acid, $C_6H_4(OCH_3).COOH$, has the constitution of *para-methoxybenzoic acid*. It was first obtained in 1839 by the oxidation of anise oil, and subsequently by similar treatment from the oils of tarragon, fennel, star-anise, etc., all of which contain *anethol* or anise-camphor, $C_6H_4(OH)C_3H_5{}^p$, which yields anisic acid on oxidation.[1]

Anisic acid may also be prepared by several synthetical reactions.

Anisic acid forms long monoclinic needles or prisms melting at 185°, and boiling at 280°. It is soluble in about 2500 parts of cold water, tolerably soluble in boiling water, and readily in alcohol.

When heated with hydriodic or concentrated hydrochloric acid, or when fused with caustic potash, anisic acid is converted into para-hydroxybenzoic acid. When distilled with caustic baryta, it is decomposed into anisol and carbon dioxide.

The sodium salt and phenyl ester of anisic acid are employed in the treatment of neuralgia and rheumatism.

HYDROXY-PHENYL-ACETIC ACIDS. $C_6H_4(OH).CH_2.COOH$. The ortho-modification melts at 137°, the meta- at 129°, and the para- at 148°. The last-named has been found in urine, and is formed in the putrefaction of albumin and synalbin. All three isomers give a violet coloration with ferric chloride. When heated with lime they yield carbon dioxide and the corresponding isomer of cresol, $C_6H_4(OH).CH_3$.

HYDROXY-TOLUIC ACIDS.

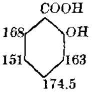
Ten modifications of hydroxy-toluic acid are possible and all have been prepared. The following arrangement shows the

iodide by distillation, and the high-boiling portion saponified with caustic soda. The acid is then liberated by hydrochloric acid, and purified from admixed salicylic acid by boiling with excess of milk of lime, and filtering from the nearly insoluble basic calcium salicylate. From the filtrate the methyl-salicylic acid is precipitated by excess of hydrochloric acid.

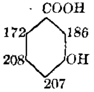
[1] Anisic acid may be conveniently prepared by pouring 1 part of oil of anise into a solution of 5 parts of potassium bichromate in 10 parts of sulphuric acid diluted with 20 of water, and heated to 50°. When the reaction is complete, which is the case in a few minutes, the liquid is allowed to cool, and the anisic acid which separates out removed by filtration. It is purified by solution in ammonia and reprecipitation by hydrochloric acid.

melting-points of these isomers. Thus the acid having the COOH, OH, and CH_3 groups in the positions 1 : 2 : 3 melts at 163°, while when the methyl group occupies the para-position, the other groups remaining as before, the compound melts at 174.5°.

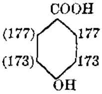
ORTHO-DERIVATIVES.



META-DERIVATIVES.



PARA-DERIVATIVES.



These hydroxy-toluic acids which have the hydroxyl group in the *ortho*-position (1 : 2) in reference to carboxyl are true homologues of salicylic acid, and are known as *homosalicylic* or *cresotic acids.*[1] They give a violet coloration with ferric chloride, dissolve with facility in cold chloroform, and volatilise readily in a current of steam. The cresotic acids are liable to occur as objectionable impurities in commercial salicylic acid (see page 104).

Of the four acids having the carboxyl and hydroxyl groups in the *meta*-position (1 : 3) relatively to each other, three give pale brown precipitates with ferric chloride, soluble more or less readily in excess of the reagent to dark brown solutions. The 1 : 3 : 4 acid gives no reaction with ferric chloride. The meta acids are not attacked by heating with concentrated hydrochloric acid at about 200°, but yield cresols when heated with lime. They are volatile with difficulty or not at all (1 : 3 : 5 acid) in a current of steam.

The two homologues of *para*-hydroxybenzoic acid crystallise in small needles containing $\frac{1}{2}H_2O$, which become anhydrous at 100°. They volatilise more or less in a current of steam, but give no reaction with ferric chloride and are not soluble in cold chloroform.

When the hydroxy-toluic acids are heated with lime they yield cresols, the particular isomer formed depending on the relative positions of the hydroxyl- and methyl-groups in the acid. When these are adjacent the product is ortho-cresol; when as 1 : 3, meta-cresol; and when opposite, para-cresol.

The following table exhibits the leading characters of the isomeric hydroxy-toluic acids:—

[1] Some chemists in expressing the constitution of the hydroxy-toluic acids, assign a constant position 1 to the methyl-group, following with the hydroxyl and carboxyl groups in the order named. Such a plan materially alters the nomenclature of the acids, and fails to exhibit the analogy of properties and reactions set forth in the text.

ISOMERIC HYDROXY-TOLUIC ACIDS.

Acid. COOH:OH:Me.	Melting Pt., ° C.	On Heating with Hydrochloric Acid.	Reaction with Ferric Chloride.	Solubility in Cold Chloroform.	Crystalline Form.	M. Pt., of Methyl Derivatives.	Observations.
Ortho-.							
1 : 2 : 3	163	*o*-cresol at 210°.	Deep violet colour.	Readily.	Long flat needles or rhombic prisms.	81°	*β*-cresotic acid; poisonous.
1 : 2 : 4	174.5	*m*-cresol at 170°.	Deep violet colour.	Moderately.	Hard white needles or prisms.	103°	*γ*-cresotic acid.
1 : 2 : 5	151	*p*-cresol at 180°.	Violet-blue colour.	Readily.	Long needles and rhombic prisms.	67°	*α*-cresotic acid; gives *o*-cresol on heating with lime.
1 : 2 : 6	168	*m*-cresol at 200°.	Blue-violet colour.	Readily.	Long needles.		
Meta-.							
1 : 3 : 2	186	Not attacked at 210°.	Bulky light brown ppt.	Slight.	Long vitreous needles.	146°	Gives *o*-cresol when heated with lime.
1 : 3 : 4	207	Not attacked at 270°.	No reaction.	Insoluble.	Long needles.	156°	Gives *o*-cresol when heated with lime.
1 : 3 : 5	208	Not attacked at 230°.	Fawn ppt. dissolving in excess with dark brown colour.	...	Stellate groups of *needles*.	93°	Symmetrical hydroxytoluic acid. *Gives m-cresol* when heated with lime. Not volatile with steam.
1 : 3(5)6(2)	172	Not attacked at 220°.	Light brown ppt. sol. in much water.	Nearly insoluble.	Prisms and needles.		...
Para-.							
1 : 4 : 2(6)	177	*m*-cresol at 200°.	None.	Insoluble.	Small needles containing ½ aqua.	176°	...
1 : 4 : 3(5)	173	*o*-cresol at 180°.	None.	Insoluble.	Small needles containing ½ aqua.	193°	...

CRESOTIC ACID, $C_6H_3(CH_3)(OH).COOH$, may be prepared from cresol by Kolbe's method for the manufacture of salicylic acid from phenol, the modification of cresotic acid obtained depending on the isomer of cresol employed for the process. It is to the presence of cresols in the carbolic acid employed in Kolbe's process that the contamination of commercial salicylic acid by the isomeric cresotic acids is due (page 65). The three isomers of cresotic acid present a close resemblance to salicylic acid and to each other, but differ in their melting-points, therapeutic action and the modification of the cresol yielded on heating under pressure with hydrochloric acid or distillation with lime.

According to M. Charteris (*Pharm. Jour.* [3], xxi, 436), meta-cresotic acid is devoid of physiological action, but both the ortho- and para- modifications possess marked toxic properties. Charteris found paracresotic acid to produce marked paralytic symptoms in rabbits when injected hypodermically, the effect becoming more marked when the poison was given in conjunction with salicylic acid, 10 grains of the mixture causing convulsions and death.

The foregoing conclusions of Charteris have had grave doubt thrown on them by the observations of others. Thus Egasse has drawn attention to the advantages of paracresotic acid as an antipyretic. Demme regards it as inferior to salicylic acid as an antipyretic, but free from some of the objections to the latter, being better tolerated by the digestive organs. Demme considers paracresotic acid the most effectual and least objectionable of the three isomers. Metacresotic acid he regards as less active, while orthocresotic acid possesses decided toxic properties, causing paralysis of the cardiac muscle. According to Demme, also, the observed ill effects are attributable to the presence of orthocresotic acid in the preparations used. Sodium paracresotate may be taken to the extent of 3 to 4 grammes without any ill effect resulting. It did not influence the temperature or occasion gastric disturbance (*Bull. Therap.*, cxxii, 85; abst. *Pharm. Jour.* [3], xxii, 694).

A solution of cresotic acid has received application as a beating liquid in tanneries. It is stated to have the advantage over other acids of exerting an antiseptic action on the skins, and so preserving instead of destroying them (J. Hauff, *J. S. C. I.*, 1889, p. 954). As it rapidly and easily dissolves the lime salts, it softens and swells the hides in a very satisfactory manner.

DIHYDROXYBENZOIC ACIDS AND THEIR ALLIES.

By the substitution of two hydroxyl-groups for two of the remaining hydrogen atoms of the benzene-nucleus in benzoic acid, a series of dihydroxyphenyl-carboxylic or dihydroxy benzoic acids are obtained, of which protocatechuic acid is the type.

The dihydroxybenzoic acids may be obtained (among other reactions) by heating the corresponding dihydroxybenzenes (hydroxyphenols) with solutions of alkali-metal carbonates, the reaction occurring with much greater facility than the formation of salicylic acid by Kolbe's process (page 65). By further heating, the dihydroxyhenzoic acids split up into the corresponding hydroxyphenols and carbon dioxide.

ISOMERIC DIHYDROXYBENZOIC ACIDS. $C_6H_3(OH).(OH).COOH$.

	ACID.	COOH : OH : OH	M.PT. °C.	COLOUR WITH FERRIC CHLORIDE.	PHENOLIC PRODUCT ON HEATING.
Ortho-hydroxyphenyl-carboxylic Acids..	Protocatechuic.	1 : 3 : 4	190	Green.	Catechol.
	Catechol-carboxylic.	1 : 2 : 3	199	Blue.	Catechol.
Meta-hydroxyphenyl-carboxylic Acids ..	α-Resorcylic.	1 : 3 : 5	222 (233)	No colour.	Resorcinol.
	β-Resorcylic.	1 : 2 : 4	213	Dark-red.	Resorcinol.
	γ-Resorcylic.	1 : 2 : 6	148 (with decomposition)	Violet; blue with excess.	Resorcinol.
Parahydroxyphenyl-carboxylic Acid	Gentisinic, or hydroxysalicylic.	1 : 2 : 5	196–200	Blue.	Hydroquinol

Protocatechuic Acid. Ortho-Dihydroxybenzoic Acid.

$$C_7H_6O_4;\ i.\ e.,\ C_6H_3\begin{cases}(^1)COOH\\(^3)OH\\(^4)OH\end{cases}$$

Protocatechuic acid occurs naturally in the fruit of *Illicium religiosum*. It results from the fusion of various organic bodies with caustic alkalies. Catechin and maclurin by similar treatment yield phloro-glucol. Many resins give para-hydroxybenzoic acid in addition, while gum benzoïn gives protocatechuic and benzoic acids. The largest yield of protocatechuic acid is stated to be

obtainable from gum kino (*Annalen*, clxxvii, 188). It may be prepared synthetically by heating catechol to 130° with a solution of sodium or ammonium carbonate. On dry distillation or when heated to 330° to 350° with caustic potash or soda, the reverse action occurs, the protocatechuic acid splitting up into catechol and carbon dioxide.

Protocatechuic acid forms thin monoclinic prisms or tufts of needles containing one molecule of water, which is lost at 100°. It melts when quite anhydrous at 190°, and at a higher temperature is resolved into carbon dioxide and catechol, $C_6H_4(OH)_2$. Protocatechuic acid dissolves in 53 parts of cold water, and in 3½ parts at 80°. It is very soluble in alcohol, less so in ether, and almost insoluble in benzene, even when boiling. It is extracted from its aqueous solution by agitation with ether or petroleum-ether.

An aqueous solution of protocatechuic acid is coloured an intense bluish-green by ferric chloride (avoiding excess), the colour being changed to blue and afterwards to dark red on adding a very dilute solution of sodium carbonate. A neutral solution of a protocatechuate gives a violet coloration with ferrous sulphate.

Protocatechuic acid gives a white precipitate with lead acetate, and reduces ammonio-nitrate of silver when heated, but has no effect on Fehling's solution.

On boiling protocatechuic acid with aqueous arsenic acid it yields *diprotocatechuic acid*, $C_{14}H_{10}O_7$, a body closely resembling digallic acid (tannin) but giving a green coloration with ferric chloride.

The salts of protocatechuic acid are unimportant, but the esters, vanillic acid, piperonylic acid, and veratric acid have some interest (page 107).

Catechin, $C_{18}H_{18}O_8$, from catechu; *maclurin*, $C_{13}H_{10}O_6+H_2O$, from *Morus tinctorea;* and *luteolin*, $C_{15}H_{10}O_6$, from *Reseda luteola*, appear to be phloroglucyl esters of protocatechuic acid.

Homologues of Protocatechuic Acid.

Besides the important class of tannins giving green colorations with ferric salts (Vol. I, Part i), the following homologues and derivatives of protocatechuic acid have a practical interest:—

NAME.	FORMULA.	M.PT., °C.	COLORATION WITH FERRIC CHLORIDE.
Orsellinic Acid.[1] Dihydroxy-*p*-toluic Acid ..	$C_6H_2(CH_3)\left\{\begin{array}{l}{}^1\,CO.OH\\ {}^2\,OH\\ {}^6\,OH\end{array}\right.$	176	Violet.
a-Homoprotocatechuic Acid	$C_6H_3\left\{\begin{array}{l}{}^1\,CH_2.CO.OH\\ {}^3\,OH\\ {}^4\,OH\end{array}\right.$	127	Green.
Isovanillic Acid. *p*-Methyl-protocatechuic Acid....	$C_6H_3\left\{\begin{array}{l}{}^1\,CO.OH\\ {}^3\,OH\\ {}^4\,O.CH_3\end{array}\right.$	250	
Vanillic Acid. *m*-Methyl-protocatechuic Acid....	$C_6H_3\left\{\begin{array}{l}{}^1\,CO.OH\\ {}^3\,O.CH_3\\ {}^4\,OH\end{array}\right.$	211	No colour.
Vanillin. *m*-Methylproto-catechuic Aldehyde	$C_6H_3\left\{\begin{array}{l}{}^1\,CO.H\\ {}^3\,O.CH_3\\ {}^4\,OH\end{array}\right.$		Bluish-violet.
Piperonylic Acid. Methylene-protocatechuic Acid	$C_6H_3\left\{\begin{array}{l}{}^1\,CO.OH\\ \left.\begin{array}{l}{}^3\,O\\ {}^4\,O\end{array}\right\}CH_2\end{array}\right.$	228	
Piperonal. Methylene-protocatechuic Aldehyde...	$C_6H_3\left\{\begin{array}{l}{}^1\,CO.H\\ \left.\begin{array}{l}{}^3\,O\\ {}^4\,O\end{array}\right\}CH_2\end{array}\right.$	37	
Veratric Acid. Dimethyl-protocatechuic Acid....	$C_6H_3\left\{\begin{array}{l}{}^1\,CO.OH\\ {}^3\,O.CH_3\\ {}^4\,O.CH_3\end{array}\right.$	179	No colour.

Vanillin. $C_8H_8O_3$; *i. e.*, $C_6H_3\left\{\begin{array}{l}COH^{(1)}\\ O.CH_3{}^{(3)}\\ OH^{(4)}\end{array}\right.$

Vanillin is the aldehyde of vanillic or methylprotocatechuic acid. It is the chief odoriferous principle of vanilla pods or *vaniloes*, the fruit of *Vanilla planifolia*, from which it was isolated in 1858. It also occurs in traces in cloves, beetroot, Siam benzoin, asafœtida, and asparagus, while its presence in the

[1] ORSELLIC ACID, $(OH)_2C_6H_2(CH_3).CO.OC_6H_2(OH)(CH_3).COOH$. This body, called also *diorsellinic* or *lecanoric acid*, is an anhydride of orsellinic acid, into which it is converted by boiling with water. It occurs in *Lecanora* and other lichens, and in *Roccella fuciformis* (used for the production of archil) together with *erythrin*, $C_{20}H_{22}O_{10}+1\frac{1}{2}H_2O$, which is an ether-derivative of diorcellinic acid and erythrol. (See Vol. III, Part i.)

wood of certain trees has been frequently noted. (See Von Lippmann, abst. *J. C. S.*, lxxxviii, i. 66.)

Vanillin is now produced artificially on a considerable scale, by a variety of methods, some of which have proved very lucrative.[1]

Practically the whole of the artificial vanillin of commerce is now made from eugenol, a phenoloid body obtained by treating oil of cloves or cinnamon-leaves with caustic alkali, filtering, and precipitating the solution with carbonic acid.[2]

Vanillin crystallises in stellate groups of colorless needles, melts at 80°–81°, and sublimes when cautiously heated. It has a pleasant aromatic taste and odour resembling vanilla. Vanillin dissolves sparingly in cold water, more freely in hot, and readily in alcohol and ether. Vanillin has the constitution and characters of an aromatic aldehyde. It forms well-defined bisulphite compounds, reduces ammoniacal silver solution, and responds to other general reactions for aldehydes. Heated with dilute hydrochloric acid (preferably under pressure to 200°) vanillin is resolved into methyl chloride and protocate-

[1] In 1876, the price of vanillin was fully £10 per ounce. At present it may be bought for 3s. or less.

The earliest patent for the artificial production of vanillin appears to have been based on the researches of Tiemann and Haarmann (*Ber.*, vii, 613). According to this process, the glucoside *coniferin*, $C_{16}H_{22}O_8 + 2H_2O$, is hydrolysed by emulsin or a dilute acid, when it yields glucose and *coniferyl alcohol*, $C_6H_3(OH)(OCH_3)(C_3H_4.OH)$, which latter body on oxidation with chromic acid mixture yields vanillin. Or the oxidation of the glucoside may be effected first and the hydrolysis afterwards. Vanillin may also be produced by the action of chloroform on a solution of guaiacol in caustic alkali, and by numerous other methods. (See German Patents, 63007, 63027, 72600, 37075, 33229; British Patent, 1892, No. 361; *Bull. Soc. Chim.*, 1898, xix, 75.)

[2] The eugenol is treated with acetic anhydride, and the acetyl-derivative oxidised by potassium permanganate. When the oxidation is sufficiently advanced, the liquid is filtered, rendered slightly alkaline, concentrated at a low temperature, acidulated with sulphuric acid, and the vanillin extracted by agitation with ether. The ethereal solution is then shaken with a solution of sodium bisulphite, and the aldehyde-compound separated, decomposed by dilute sulphuric acid, and the liberated vanillin again extracted with ether. This process has undergone various modifications, the most important of which is the conversion of the eugenol into isoeugenol by boiling with caustic alkali.

An improvement recommended by Bötringer and Söhne consists in first converting the eugenol into its benzyl ether by treatment with benzyl chloride in alcoholic solution and in presence of caustic alkali. By prolonged boiling with alcoholic potash, this is converted into *iso*-eugenol benzyl ether, which crystallises from alcohol. This product is oxidised by means of a sulphuric acid solution of sodium chromate to vanillin benzyl ether, from which vanillin is readily obtained by treating with fuming hydrochloric acid for twenty-four hours in the cold.

Vanillin may also be prepared by the action of methyl sulphate on protocatechuic aldehyde.

chuic aldehyde; and when fused with caustic potash is converted into protocatechuic acid.

By exposing moist and finely-pulverised vanillin to the air it is oxidised to vanillic or methylprotocatechuic acid, $C_8H_8O_4$, which crystallises from ether in white laminæ, and gives no colour-reaction with ferric chloride.

By reducing vanillin in dilute alcoholic solution with sodium amalgam, vanillyl alcohol, $C_6H_3(OH)(OCH_3),CH_2OH$, is produced, which forms prisms melting at 115°. Vanillin has an acid reaction and forms salts with bases.

Vanillin may be extracted from aqueous liquids containing it by acidulating and agitating with ether. It may then be separated from many substances simultaneously extracted by agitating the ethereal solution with a semi-saturated solution of sodium bisulphite.

On heating vanillin with hydrochloric acid and phloroglucol a characteristic red colour is produced.

On rubbing together vanillin, resorcinol, and hydrochloric acid, a deep bluish-violet coloration is observed, which vanishes after a time. A 1 per cent. solution of vanillin in hydrochloric acid, mixed with an equal volume of sulphuric acid, gives with a few drops of a liquid containing even 0.01 per cent. of acetone a violet colour on heating at 100° C. for 15 minutes.

If a little thiophene and concentrated sulphuric acid be added to an alcoholic solution of vanillin, the liquid acquires a green to bluish-green coloration (A. Ihl, *Chem. Zeit.*, xiv, 1707).

Besides its agreeable odour, vanillin is characterised by the bluish-violet coloration produced in its solution on addition of ferric chloride. On heating the liquid, *dehydro-divanillin*, $C_{12}H_4(OH)_2(COH)_2(OCH_3)_2$, separates in fine white needles, melting at 304°, and sparingly soluble in water, alcohol, ether, chloroform, and benzene, but readily soluble in alkalies (Tiemann, *J. S. C. I.*, v, 252).

J. Hanus has described a method of determining vanillin based on its conversion into a hydrazone of suitable properties (abst. *Analyst*, 1900, p. 318). He directs that a solution of β-naphthylhydrazine hydrochloride, $C_{10}H_7.NH.NH_2.HCl$, should be added to the aqueous solution of vanillin in such proportion that from 2 to 3 parts of the hydrazine are present for every one part of the aldehyde. After standing for five hours the precipitate is transferred to a tared filter, washed with hot water till the washings no longer reduce silver nitrate, dried at 90° C., and weighed. Divided by 1.92, the weight of the hydrazone gives that of the vanillin present. An alternative and somewhat preferable precipitant is p-bromophenylhydrazine, $C_6H_4Br.NH.NH_2$. The manipulation is the same as with β-naphthylhydrazine, but the divisor is 2.11. Hanus states that his methods are applicable

in all cases where an aqueous solution of the vanillin can be prepared, and claims that they have the advantage over Welman's method (titration with alcoholic potash) of being unaffected by the presence of vanillic acid.

A. Stocky isolated vanillin from a sample of wine-vinegar suspected to contain it, by evaporating a large volume of the liquid to dryness with calcium carbonate, extracting the residue with ether, and evaporating the ethereal solution. After repeatedly crystallising the residue thus obtained from alcohol it was identified as vanillin by the formation of a metallic mirror with an ammoniacal silver solution, and its reaction with phloroglucol and hydrochloric acid.

ISO-VANILLIN, $C_6H_3(CHO)^1(OH)^3(OCH_3)^4$, is an isomer of vanillin obtained by heating opianic acid under pressure with dilute hydrochloric acid, and is formed in small quantity, together with vanillin, in many reactions. It forms vitreous prisms which melt at 115° to a liquid boiling at 179°, yielding a vapour having an odour resembling that of vanilla and anise. Isovanillin gives no coloration with ferric chloride.

Commercial vanillin is not infrequently adulterated to a considerable extent (*e. g.*, 50 per cent.) with acetanilide (antifebrin), an addition which lowers the melting point of the sample. The admixture may be detected by heating the substance to 60° C. with a 5 per cent. solution of caustic soda, when aniline is formed and may be detected by the usual tests. A quantitative separation of vanillin and acetanilide may be effected by dissolving the mixture in ether and shaking the liquid with a concentrated aqueous solution of sodium bisulphite, which dissolves the vanillin only. The amount of acetanilide present in vanillin may also be deduced from the nitrogen in the sample (L. F. Kebler, *Amer. J. Pharm.*, 1902, p. 12).

Sugar is occasionally met with as an adulterant of vanillin. It may be detected by its insolubility in ether or chloroform.

In America, vanillin is sometimes adulterated with *benzoic acid*, and occasionally that acid simply flavoured with vanillin has been substituted for the latter substance. The two bodies may be separated by dissolving the sample in ether and shaking the liquid with sodium bisulphite solution, which will remove the vanillin, leaving the benzoic acid dissolved in the ether.

Kebler has met with vanillin adulterated with or substituted by acetyl-iso-eugenol, the direct antecedent of vanillin in its synthetic production from iso-eugenol. One adulterated sample contained only a little vanillin, added to give the characteristic odour. Acetyl-iso-eugenol melts at 78°, and vanillin at 80° to 81° C. The adulterant was detected by its crystalline form, abnormal solubility in various solvents, and by the presence of the acetyl-group. Strong sulphuric acid gave a beautiful red

colour, whereas a lemon-yellow colour is yielded by pure vanillin. The amount of vanillin was determined by the Hess and Prescott method (page 113).

VANILLA is the fruit or pod of *Vanilla planifolia*, var. *aromatica*, an orchid grown in Mexico, Bourbon, the Seychelles, Fiji, etc. Its cultivation has become to a certain extent restricted since vanillin has been produced artificially; but the superior aroma and flavour of the natural product prevent the artificial vanillin from wholly superseding it.[1]

For the determination of vanillin in vanilla, a known weight (20 to 50 grammes) of the pods should be ground up with sand, and the mixture extracted with ether. The filtered liquid is shaken with a saturated solution of sodium bisulphite, diluted with an equal volume of water, and the ethereal layer separated. The sulphite solution is then treated with dilute sulphuric acid and the sulphurous acid liberated driven off by passing a current of carbon dioxide or steam. The vanillin is then extracted from the acid liquid by agitating with ether, which is separated, cautiously evaporated, and the residual vanillin weighed. By this process, which is apt to give results somewhat below the truth, W. Busse found 2.16 per cent. of vanillin in German East African vanilla; 1.48 per cent. in Ceylon pods; and 1.55 and 2.02 per cent. in Tahiti vanilla. Tiemann and Haarmann found in the best Mexican pods 1.69 and 1.86 of vanillin; in Bourbon, 1.91 to 2.90; and in Java pods 2.75 per cent. of vanillin.

Busse holds that there is no relation between the proportion of vanillin contained in the fruit and the value of the sample for flavouring purposes, and that the aroma and flavour of vanilla are not wholly due to vanillin. Tiemann and Haarmann found that on distilling the ethereal extract of vanilla, from which the vanillin has been removed by sodium bisulphite, an oily substance of very offensive odour remained. Much less was obtained from Mexican vanilla than from Java or Bourbon pods.

In the variety of West Indian vanilla called *vanillone* the vanillin (from 0.4 to 0.7 per cent.) is associated with another substance, which is probably benzoic aldehyde. Vanillone has long been used for preparing "essence of heliotrope," but this is now made by adding a small quantity of benzoic aldehyde (artificial) to artificial vanillin, when, after some time, the mixture acquires the exact odour of the natural white heliotrope.

Some varieties of vanilla contain *vanillic acid*, which was

[1] The substance to which the odour of vanilla is due does not appear to exist in the fruit when gathered, but is developed during the "curing" operation by a process of fermentation. The greater part of the vanillin is contained in the fruit in the form of a glucoside, from which free vanillin can be obtained by the action of emulsin or dilute acids.

apparently mistaken for benzoic acid by the earlier investigators.

Inferior or exhausted vanilla is occasionally dusted over with crystals of benzoic acid, which gives it the frosted appearance regarded as characteristic of vanilla of good quality. If a little of the crystalline matter be added to an alcoholic solution of phloroglucol previously mixed with an equal measure of hydrochloric acid, a magnificent red colour is produced in presence of vanillin.

Certain species of vanilla contain *piperonal* as well as vanillin. No satisfactory method has hitherto been proposed for the separation of these two aldehydes, and any process for the estimation of vanillin in presence of piperonal must depend on the reactions of the free hydroxyl-group present in vanillin but not in piperonal. Certain colour-reactions fall under this head, *e. g.*, with mercurous nitrate, *p*-nitrodiazobenzene or ferric salts, but these are hardly applicable for quantitative purposes. Hence J. Hanus (*J. S. C. I.*, 1900, p. 935) recommends the following procedure: A volume of liquid, estimated to contain from 0.02 to 0.15 gm. of vanillin, is placed in an Erlenmeyer flask of 150 c.c. capacity, and 10 c.c. of a 10 per cent. solution of platinic chloride added. The volume is then made up to 50 c.c. with water (with more than 0.06 gm. of vanillin it may be made up to 100 c.c. if desired). The flask is then placed in a hot-water oven kept at a temperature of 70° to 80° C. and allowed to remain there for one hour. It is then removed and allowed to cool for one hour longer. The condensation-product, consisting of grey needles free from mineral matter, is then filtered off in a Gooch crucible containing a layer of asbestos; it is washed with cold water, and dried at 100° to 105° to constant weight (about three hours). The quantity of vanillin, x, is calculated from the weight of the product, y, by one of the following formulæ: $x = \frac{y + 15.7}{0.97}$ (for 50 c.c.), or $x = \frac{y + 38.25}{1.04}$ (for 100 c.c.) The presence of piperonal has very little effect on the determination of vanillin by the above method.

A. Moulin (*J. S. C. I.*, 1903, p. 514) has devised a colorimetric method for the determination of vanillin in vanilla, based upon the conversion, by nitric acid, of the $—C_6H_3.OCH_3$ group in vanillin into methyl picrate.

Essence of Vanilla. Under this name, an alcoholic extract of vanilla beans is largely employed for flavouring purposes. Much of the so-called "essence," however, is merely an alcoholic solution of artificial vanillin, coloured with caramel (sometimes with an admixture of artificial coumarin). Genuine extract of vanilla pods contains a resin of dark red or brown colour, soluble in 50 per cent. alcohol, but precipitated on further dilution.

Hence when weaker spirit is used for preparing vanilla extract, potassium bicarbonate or other alkali is used to effect solution of the resin, but the flavour of the preparation is prejudicially affected thereby. Presence of resin, as indicated by precipitation on dilution with water, is more or less indicative of a genuine extract, whereas the presence of caramel and coal-tar dyes points to the vanillin being artificial.

An imitation extract of vanilla made from Tonka beans is sometimes substituted in America for true vanilla extract. H. Leffmann distinguishes between the two by evaporating the extract on the water-bath, redissolving the residue in a little water, acidulating the solution slightly, and shaking with ether. The residue left on evaporating the ethereal layer is mixed with a very small amount of phloroglucol and a drop of hydrochloric acid and the mixture heated on the water-bath. Vanillin gives a red coloration, but coumarin does not. This test would not serve for the detection of Tonka beans in admixture with vanilla.

For the separation of *vanillin* and *coumarin*, as requisite in the analysis of mixed extracts of vanilla and Tonka beans, Hess and Prescott (*Jour. Amer. Chem. Soc.*, 1899, p. 256) recommend the following process:—A weight of from 25 to 100 grammes of the extract is evaporated at 80°, water being added at intervals to keep the volume of the liquid constant until the alcohol has volatilised. Lead acetate is then added with agitation as long as a precipitate forms, when the liquid is filtered through asbestos and the precipitate washed with a little hot water. The cooled filtrate is agitated with ether, and the ethereal layer separated and agitated with dilute ammonia. This extracts the vanillin, while the coumarin remains dissolved in the ether, which is allowed to evaporate spontaneously. The residual coumarin is purified by solution in petroleum-ether, and finally weighed. The melting-point (67°) and characteristic odour are sufficient for its identification. The vanillin may be recovered by slightly acidulating the ammoniacal solution with hydrochloric acid, extracting with ether, and evaporating cautiously. After purification by solution in boiling petroleum-spirit, the product should be pure vanillin, melting at 80° to 81°. After weighing, colour-tests may be applied for the identification of of vanillin, bearing in mind that phenoloid bodies giving colorations with ferric salts are liable to be present. Chloroform may be advantageously substituted for ether in the above process, which Hess and Prescott consider preferable to the bisulphite method.

Winton and Silvermann (*J. Amer. Chem. Soc.*, xxiv, 1128) recommend the above process, but use a 2 per cent. solution of ammonia instead of 10 per cent. as prescribed by Hess and

Prescott, and they also prefer to weigh the vanillin and coumarin before dissolving in petroleum-spirit. Any insoluble matter, which is usually insignificant in amount, may afterwards be weighed separately and allowed for if necessary. Six extracts prepared by Winton and Silvermann from different grades of vanilla pods by the formula of the U. S. Pharmacopœia (100 grammes of pods per litre of extract) had a specific gravity ranging from 1.0104 to 1.0166, and contained vanillin, from 0.06 to 0.22 per cent., and cane-sugar, about 20 per cent. Details of the method of analysis are given (*J. S. C. I.*, 1902, p. 1300), and a further improvement of the process employed has been described by Winton and Bailey, *J. Amer. Chem. Soc.*, 1905, xxvii, 719; abst. *Analyst*, xxx, 275.

The following colorimetric method has been proposed by Mœrk (*Amer. Jour. Pharm.*, lxiii, 572) for the rough assay of *essence of vanilla*:—

The vanilla-extract is treated with freshly-precipitated lead hydroxide and to an aliquot part of the filtrate, after dilution, bromine-water is added, drop by drop, until the colour of bromine no longer disappears on shaking the liquid. By careful addition of a 1 per cent. solution of ferrous sulphate a bluish-green colour is developed, which gradually increases in intensity to a maximum. By comparing this colour with that produced in a solution of known vanillin content, the estimation of the quantity of the vanillin in the extract may be effected.

Piperonal. $C_8H_6O_3$; *i. e.*, $C_6H_3\left\{\begin{array}{l}(1)CO.H \\ \left.\begin{array}{l}(3)O \\ (4)O\end{array}\right\}:CH_2\end{array}\right.$

Piperonal, or *heliotropin* as it is commercially named, has the constitution of *methylene-protocatechuic aldehyde*. It was originally produced by the gradual addition of a solution of potassium permanganate to one of potassium piperate obtained by the saponification of piperine, the alkaloid of pepper. The liquid acquires a pleasant odour like that of coumarin, and yields piperonal on distillation.

Piperonal is manufactured from *safrol*, $C_6H_3(C_3H_5)^1(O_2.CH_2)^{3:4}$, a leading constituent of the oils of sassafras and camphor. By the action of caustic alkali the safrol is first isomerised to *iso-safrol*, and 5 parts of this are treated with a reagent made by dissolving 25 parts of potassium bichromate in 38 parts of strong sulphuric acid and 80 parts of water. The product of the reaction is distilled in a current of steam, the distillate extracted with ether, and the dissolved piperonal purified by conversion into its bisulphite compound. Piperonal crystallises in large lustrous prisms or thin plates. It has a very pleasant odour, closely resembling that of the heliotrope,

and on this account is extensively employed in perfumery under the name of "heliotropin." Piperonal is very sparingly soluble in cold water, but more readily in hot, and dissolves very easily in alcohol and ether. It has the general characters of an aldehyde. Its compound with sodium bisulphite crystallises in laminæ and is but slightly soluble in water or alcohol. By treatment with oxidising agents or boiling with alcoholic potash piperonal is converted into *piperonylic acid* (page 107), while on reduction of its boiling aqueous solution by sodium amalgam it yields *piperonyl alcohol*, $C_6H_3.(O_2:CH_2).CH_2OH$, a sparingly soluble body melting at 51°.

When heated under pressure to 200° C., with dilute hydrochloric acid, piperonal is decomposed into protocatechuic aldehyde and finely divided carbon.

In doses of 0.5 to 1.0 gramme, piperonal has been employed as an antiseptic and antipyretic of moderate power, but some observers find it to be devoid of physiological action. By far its most important application is in perfumery.

Piperonal is injuriously affected by exposure to a temperature above or approaching its melting-point, and is preferably preserved in alcoholic solution. It is liable to the same kinds of adulteration as vanillin, and, in addition, to contain an admixture of vanillin itself.

GALLIC ACID AND ITS ALLIES.

Of the six possible compounds having the constitution of trihydroxybenzoic acids, the three following isomers are well-known:—

Gallic Acid.	Pyrogallol-Carboxylic Acid.	Phloroglucol-Carboxylic Acid.
$C_6H_2 \begin{cases} COOH(1) \\ OH(3) \\ OH(4) \\ OH(5) \end{cases}$	$C_6H_2 \begin{cases} COOH(1) \\ OH(2) \\ OH(3) \\ OH(4) \end{cases}$	$C_6H_2 \begin{cases} COOH(1) \\ OH(2) \\ OH(4) \\ OH(6) \end{cases}$

Of these compounds, gallic acid is the only one of practical interest.[1]

[1] Pyrogallol-carboxylic acid is obtained when pyrogallol is heated with potassium hydrogen carbonate (*Ber.*, xviii, 3205). It decomposes when heated to 195°, but may be sublimed without decomposition in a current of carbon dioxide. The solution gives a violet coloration with ferric chloride.

Phloroglucol-carboxylic acid is obtained by boiling phloroglucol with an aqueous solution of potassium carbonate. It decomposes at 100° or when boiled with water into phloroglucol and carbon dioxide.

Gallic Acid. $C_6H_2(OH)_3 . COOH + H_2O$.

Gallic acid occurs naturally in the free condition in gall-nuts, tea, sumac, divi-divi, mangoes, pomegranates, and many other plants, and may be obtained artificially by fusing brom-hydroxybenzoic acid or bromo-protocatechuic acid with potassium hydroxide. It is usually prepared, however, by the action of boiling dilute sulphuric acid on ordinary tannic acid (tannin), or, as it is frequently termed, gallotannic acid.[1] In this reaction one molecule of tannic acid is hydrolysed, taking up a molecule of water, with the formation of two molecules of gallic acid:—

$$\underset{\text{Digallic or Tannic Acid.}}{C_{14}H_{10}O_9} + H_2O = \underset{\text{Gallic Acid.}}{2C_7H_6O_5}.$$

As in the case of many other reactions of a hydrolytic nature, the same result may be brought about by the action of a natural ferment. The body which most readily acts in this sense is the nitrogenised ferment contained in gall-nuts.[2] To bring about this change, the powdered galls are moistened with water and exposed to the air for several weeks. The dark-coloured mass is washed with a little cold water and then boiled with more water, which extracts the gallic acid.

Gallic acid occurs in the form of acicular prisms or silky needles, either white or, generally, of a faint buff colour, containing one molecule of water of crystallisation. It is odourless, and possesses a faintly acid taste. It loses its water of crystallisation at 100°. (Böttinger states that gallic acid does not become anhydrous below 120°, but this is apparently an error.)

[1] The tannin extract is introduced, in a crude state, into a lead-lined vacuum pan, together with the necessary quantity of sulphuric acid, and the whole is heated to about 50° to 65° C. in a vacuum of 500 mm. Nearly the whole of the gallotannic acid is converted into gallic acid, and the concentration is kept up by the reintroduction of spent mother-liquor from the crystallising pans. Under these conditions the brown amorphous products obtained when the operation is conducted in open vessels are no longer formed; and, after the reaction is complete, the liquor can be concentrated until the gallic acid begins to separate by crystallisation. The crude product is in the form of handsome yellow crystals, which furnish a perfectly pure, colourless acid on double crystallisation in presence of animal charcoal free from lime.

[2] A. Fernbach (*Compt. rend.*, Dec. 24, 1900) assumes that it is the mould-fungi formed in the gallic acid fermentation which bring about the hydrolysis of the tannin by a special ferment, *tannase*. Fernbach isolated this enzyme by cultivating *Aspergillus niger* in Raulin's liquid containing tannin in place of sugar. By precipitation with alcohol, H. Pattevin (*loc. cit.*) obtained tannase as a grey powder, the neutral or acidulated solution of which is much more active than the original liquid. It acts most powerfully at 67°, is contained in sumac leaves, and appears to be widely distributed in the vegetable kingdom.

When heated to a temperature of 210° to 220° C., gallic acid melts and decomposes with formation of carbon dioxide and *pyrogallol*, $C_6H_6O_3$, which latter body can be obtained as a sublimate. If the temperature be raised rapidly to 250°, water is given off in addition to carbon dioxide, and in the retort is found a considerable proportion of a deep-coloured, lustrous substance, which consists chiefly of *metagallic acid*, $C_6H_4O_2$.

Gallic acid is soluble in about 100 parts of cold or 3 parts of boiling water. The hot solution deposits abundant crystals of the hydrated acid on cooling. Gallic acid is soluble in 5 parts of 90 per cent. alcohol, in 40 parts of ether, and in 12 of glycerol.[1]

An aqueous solution of gallic acid has an acid and astringent taste and readily undergoes decomposition. Gallic acid may be extracted from its aqueous solution by agitation with ether or ethyl acetate.

Gallic acid is monobasic and forms a series of well-defined, but unimportant, crystallisable metallic salts. The gallates of the alkali-metals are stable in the dry state, or in acid solution, but in alkaline solution they readily absorb oxygen and become coloured, owing to the formation of *galloflavin*, a yellow dye of the xanthone series. Basic bismuth gallate is described on page 123.

Oxidising agents, such as arsenic acid and iodine, convert gallic acid into *ellagic acid*, which is probably a fluorene derivative.

According to Guignet (*Compt. rend.*, cxiii, 200), when a warm solution of gallic acid is added to a warm mixture of zinc-powder and ammonia, it is completely converted into benzoic acid after being heated to 60° for some hours. Benzoic acid is also formed when gallic acid is heated with zinc and dilute sulphuric acid, but in this case the benzoic acid remains undissolved.

When gallic acid is heated with five times its weight of strong sulphuric acid to 100°, it is converted into *rufigallic acid*, $C_{14}H_8O_8$.

[1] The following table, based on the observations of Rosenheim and Schidrowitz (*Trans. Chem. Soc.*, 1898, p. 882) shows the solubility of gallic acid in 100 parts of various solvents at 15° C.:—

Solvent.	Parts of Gallic Acid Dissolved.	Solvent.	Parts of Gallic Acid Dissolved.
Acetone	29.4	Mixed benzene and ethyl acetate (1:1)	0.77
Acetone + 5% water.	22.2	Ether (anhydrous)	2.5
Alcohol (absolute)	22.2	Ether (moist)	2.7
Alcohol (90%)	18.9	Sodium chloride (26.9%)	0.96
Ethyl acetate	8.4	Water (at 12.5°)	0.76

The liquid first becomes red and next purple, and if then poured into water, nearly pure rufigallic acid is precipitated.[1] If, in the above process, a portion of the gallic acid be replaced by benzoic acid, the product is *anthragallol*, one of the isomeric trihydroxy-anthraquinones.

Gallic acid is absorbed by certain organic tissues, such as hide and silk, in the same manner as tannic acid, but far less readily and completely. Vignon (*Compt. rend.*, 1895, p. 916) states that ungummed silk absorbs from 7 to 8 per cent. of its weight from a 4 per cent. solution of gallic acid at a temperature of 80°; but with a bath of 1 per cent. strength the absorption is practically *nil*. From a mixed bath of tannic and gallic acids the former is preferentially absorbed.

Gallic acid and its derivatives are used to a considerable extent in medicine. Gallic acid is also used as a reducing agent in photography and is a constituent of certain hair-dyes. It finds considerable employment in the manufacture of pyrogallol (page 124).

Analytical Reactions of Gallic Acid.

An aqueous solution of gallic acid gives the following reactions:—

On the addition of a solution of ferric chloride a deep blue precipitate is formed, which is soluble in excess of the reagent with green colour. The exact colour of the precipitate is much affected by the concentration of the solutions. An excess of gallic acid destroys the colour, and reduces the iron to the ferrous state. A similar change occurs on boiling the liquid.

In the absence of air, a solution of ferrous sulphate gives a white precipitate with a concentrated solution of gallic acid. With a dilute solution no immediate reaction occurs, but on exposure to air the liquid becomes bright blue, and deposits a black precipitate without becoming decolorised.

[1] Rufigallic acid, or Rufigallol, is a *hexahydroxyanthraquinone* of the constitution:—$C_{14}H_2O_2(OH)^1(OH)^2(OH)^3(OH)^5(OH)^6(OH)^7$. It forms small, shining, reddish-brown crystals containing 2 aqua, but becomes anhydrous at 220°, and sublimes at a higher temperature in cinnabar-red prisms. Rufigallic acid dissolves sparingly in hot water, alcohol, and ether. It dissolves with an indigo-blue colour in caustic alkalies, and gives an indigo-blue precipitate with baryta-water. When heated with zinc-dust it is reduced to anthracene, $C_{14}H_{10}$.

When pyrogallol is fused with ammonium oxalate it yields ammonium *rufigallate*, which dissolves in water with red colour, and gives the following reactions:—Potassium ferricyanide and potassium bichromate give a dark brown precipitate insoluble in alcohol. Ferric chloride gives no black coloration, and neither sodium nitroprusside nor platinic chloride produce either precipitate or change of colour. On adding a few drops of acetic acid, and then potassium cyanide and mercurous nitrate, a black precipitate is obtained. Caustic alkalies cause a change to brown but not to black.

W. H. Ince (*Pharm. Journ.* [3], xvii, 462) prepares a neutral solution of ferrous chloride by decomposing cupric chloride by iron-filings or wire. He adds this reagent to the solution to be tested for gallic acid, and then gradually adds bromine in excess. Operating in this manner, gallic acid gives a faint blue colour on first adding the ferrous chloride, and this is changed to indigo-blue on cautious addition of bromine-water or vapour, but the liquid is decolorised on adding excess.

On addition of excess of caustic alkali to a solution of gallic acid the liquid turns yellow and ultimately brown and black on exposure to the air, from formation of tanno-melanic acid. The reaction is accelerated by boiling. On neutralising the black liquid with acetic acid and adding lead acetate, a black precipitate is thrown down. If sodium bicarbonate be used instead of caustic alkali, the liquid becomes indigo-blue and deposits a deep bluish-green precipitate, turned red by acids.

Lime-water in excess produces a white precipitate with solutions of gallic acid, changing very rapidly to blue.

When ammonium chloride and ammonia are added to a solution of gallic acid no precipitate is formed, but a strong red colour is developed if the solution is strong, or a greenish coloured ring at the junction of the layers of the liquids is formed, if the solution be weak.

A red colour is produced in solutions of gallic acid by chlorine-water and ammonia.

With a solution of potassium antimony tartrate, gallic acid yields a white precipitate even in very dilute solutions, and the filtrate is practically free from gallic acid. The reaction is prevented by ammonium chloride or acetate. Precipitation as gallate has been proposed as a means of determining antimony.[1]

Gallic acid reduces Fehling's solution only slowly and imperfectly, with formation of acetic and pyrotartaric acids and other products (C. Böttinger, *J. S. C. I.*, x, 480). Gallic acid reduces gold and silver solutions (rapidly when hot), and decolorises an acid solution of potassium permanganate, being oxidised to hydro-rufigallic acid, $C_{14}H_8O_5$.

In the absence of other reducing agents, gallic acid may be determined by titration in an acid solution with permanganate, preferably in presence of indigo. If tannic acid be present, it must first be separated by precipitation with gelatin.

No precipitate (distinction from tannic acids) is produced with gallic acid by solutions of alkaloids, gelatin, albumin, or starch, but a mixture of gum-arabic and gelatin is precipitated.

According to Griggi, a 3 per cent. solution of potassium

[1] The British Pharmacopœia (1898) erroneously states that gallic acid is not precipitated by tartarated antimony.

cyanide produces, with a 1 per cent. solution of gallic acid, a fine ruby-red coloration, which shortly disappears, but can be restored by agitating the liquid. Tannic acid and pyrogallol give a yellowish-red colour when similarly treated. If hydrogen peroxide be added in addition to potassium cyanide, gallic acid still gives a ruby-red coloration; but with tannic acid the colour is yellowish-brown, and with pyrogallol a dirty white turbidity is produced.

The following table exhibits the reactions of gallic acid in juxtaposition with those of gallotannic and pyrogallic acids, to which bodies gallic acid presents many points of resemblance:—

Reagent.	One per Cent. Solution of:		
	Gallotannic Acid.	Gallic Acid.	Pyrogallol.
1. Gelatin	White or buff coloured precipitate.	No change, except in presence of gum-arabic.	No change.
2. Ferrous sulphate (free from ferric salt)	No change; white in concentrated solution, darkening on exposure.	No change; white in concentrated solution, darkening on exposure.	White precipitate, changed to blue solution by least trace of ferric salt.
3. *Ferric chloride*	*Blue-black ppt.*; colour destroyed by boiling.	*Deep blue coloration*, destroyed by boiling.	*Red colour, turning* brown on heating.
4. Ferric acetate	Blue-black ppt.	Purple-black ppt.	Purple-black colour.
5. Ammoniacal ferricyanide	Deep red coloration destroyed by moderate excess of the reagent.	Vermilion-red coloration, only destroyed by a large excess of reagent.	Intense brown colour.
6. Ammoniacal picric acid	Reddish.	Red coloration, rapidly changing to fine green.	Reddish colour.
7. Lime-water in excess; or barium chloride and ammonia	White precipitate, rapidly becoming blue.	White precipitate, very rapidly becoming blue.	No ppt.; immediate purple colour becoming brown in *the air.*
8. Lead acetate	White ppt. insoluble in acetic acid.	White ppt., soluble in acetic acid.	Slight precipitate.
9. Lead nitrate	White precipitate.	No change.	No change.
10. Tartar-emetic	White ppt. insoluble in ammonium chloride.	White ppt. soluble in ammonium chloride.	No change.
11. Bismuth nitrate	White precipitate.	Pale yellow ppt.	Dark greenish ppt.
12. Ammoniacal cupric sulphate	Precipitate.	No precipitate.	Deep purple-brown coloration.
13. Potassium cyanide	Yellowish-red.	Ruby-red colour, disappearing on standing, but restored by shaking with air.	Yellowish-red.

With Hübl's iodine solution, gallic acid yields a golden-yellow substance which is readily soluble in water. Tannic acid absorbs less iodine than gallic acid, and gives a yellow, granular product which is nearly insoluble in water.

An ammoniacal solution of potassium ferricyanide produces with gallic acid a very bright red coloration, destroyed only on adding a large excess of the reagent.

An aqueous solution of picric acid, to which an excess of ammonia has been previously added, produces with gallic acid a red coloration, changing in a few seconds to a beautiful green.

Gallic acid gives a somewhat similar and delicate reaction on addition of a faintly alkaline solution of sodium arsenate, when the surface of the liquid exposed to the air rapidly becomes deep green.

When gallic acid mixed with twice its weight of phenylhydrazine is heated to 100°, or a slightly higher temperature, and then boiled with water, or when the aqueous solutions of the two substances are mixed and boiled, a compound is obtained which dissolves in very dilute caustic soda solution with reddish-yellow, orange, or golden coloration. Tannin, on similar treatment, yields a splendid greenish-blue solution, gradually turning yellow (C. Böttinger, *Annalen*, cclvi, 341).

W. P. Dreaper (*J. S. C. I.*, 1893, xii, 412) has devised a process by which gallic acid can be determined volumetrically with very fair accuracy. It consists in heating the solution to be tested to about 90° C. and adding about one gramme of precipitated barium carbonate, free from calcium.[1] A solution of copper sulphate containing 30 grammes of the crystallised salt per litre is then added with agitation until the precipitate shows a tendency to collect at the bottom of the liquid. A drop of the supernatant liquid is then removed and placed on about a square inch of filter-paper, to the other side of which a drop of solution of potassium ferrocyanide is applied. If the reaction is complete a faint pink coloration will be observed, owing to the formation of cupric ferrocyanide. If no colour is obtained, more copper sulphate must be cautiously added and the testing of a drop of the liquid repeated. Dreaper found 0.5 gramme of the purest gallic acid obtainable to require 45 c.c. of the standard copper solution for its precipitation.[2]

Gallotannic acid behaves in the above process exactly like gallic acid, except that 0.5 gramme of purest specimen obtain-

[1] The barium carbonate neutralises and precipitates the sulphuric acid set free in the process, and greatly facilitates the subsidence of the precipitate.

[2] A slight correction should be made for the excess of copper solution requisite to yield a visible reaction.

able requires only 25 c.c. of the copper solution for its precipitation. Hence where a mixture of tannic and gallic acids is to be analysed, it is necessary first to separate the former. This is effected by Dreaper by adding to 50 c.c. of the solution 5 grammes of barium sulphate, followed by 28.6 c.c. of a solution containing 20 grammes of gelatin to the litre, which should be added gradually with constant stirring. The liquid is then saturated with dry salt, and 10 c.c. of dilute sulphuric acid (1 : 20) added.[1] By this treatment tannic acid is completely precipitated, and the gallic acid can be determined by titrating 50 c.c. of the filtered liquid with copper solution, in the manner already described.

An approximate estimation of the gallic acid may be made by titrating the filtrate with standard permanganate in presence of sulphuric acid and indigo-carmine.

Another method of separating gallic acid from tannins depends on the insolubility of cupric gallate in water, and its solubility in ammoniacal liquids. The solution is precipitated by excess of cupric acetate, the precipitate washed and digested with a cold solution of ammonium carbonate. The solution, filtered from any insoluble tannate of copper, is evaporated to dryness, the residue moistened with nitric acid, ignited, and the resultant cupric oxide weighed. Its weight, multiplied by 0.9, gives the weight of gallic acid. This method is applicable to the separation of gallic acid from gallotannic and quercitannic acids, but the copper salts of many varieties of tannin are more or less soluble in ammonium carbonate.

The solubility of lead gallate in acetic acid affords another means of separating gallic and tannic acids.

In the absence of tannic acid and other substances which interfere with the reaction, gallic acid may be estimated by digesting the solution containing it with a known weight of recently-ignited oxide of zinc. The insoluble zinc powder is filtered off and washed, dried at 110°, and finally weighed. The increase in weight may be regarded as the amount of gallic acid taken up. Gallic acid may be separated from many varieties of tannin by agitating it in aqueous solution with ether. When the tannin is soluble in ether, it may be precipitated by a moderate excess of gelatin, and the gallic acid extracted from the filtrate by agitation with ether or acetic ether.

Esters and Derivatives of Gallic Acid.

A number of derivatives of gallic acid have recently found application in medicine. The following are the most important of these:—

[1] This will bring the measure of the liquid to 100 c.c.

"Dermatol" is a basic gallate of bismuth of the formula:— $C_6H_2(OH)_3.COOBi(OH)_2$.[1] It forms a soft, bright yellow, tasteless, odourless powder, which reddens litmus-paper but is almost insoluble in water, alcohol, and ether. It should be wholly soluble in dilute acids and in caustic soda solution, and should give no reaction for nitrates with diphenylamine. Dermatol is a valuable substitute for iodoform, and in doses of 0.25 to 0.5 gramme is employed internally in the treatment of diarrhœa.

"Airol," a compound of the formula $C_6H_2(OH)_3.COOBi(OH)I$, possesses at once the absorbent properties of dermatol and the antiseptic properties of its iodine. It forms a greenish-grey, odourless, tasteless powder, which loses iodine on exposure to moist air. *"Iodogallicin"* is a methyl-derivative of airol.

"Gallicin," or *methyl gallate*, $C_6H_2(OH)_3.COO(CH_3)$, is prepared by passing a current of dry hydrochloric acid gas through a solution of gallic acid in methyl alcohol. It forms fine needles or prisms which melt at 202°, and are readily soluble in water and alcohol. It is used as an antiseptic dusting powder, and in certain eye diseases.

"Bismal." Gallic acid readily condenses with formic aldehyde to form bodies typified by *methylene-digallic acid*, or *methylene gallate*, $C_6H_2(OH)_3.CO.O.CH_2.OCO.(OH)_3C_6H_2$. The *bismuth* salt of this body, said by Merck to be $4\ C_{15}H_{12}O_{10} + 3Bi(OH)_3$, is the "bismal" of commerce. It forms a bluish-grey, voluminous powder, soluble with yellow or red colour in alkalies and reprecipitated by acids. It is recommended in doses of 0.1 to 0.3 gramme as an internal astringent in chronic diarrhœa (compare *Ber.*, 1898, xxxi, 259).

"Gallobromol" is a *dibromogallic acid*, $C_6Br_2(OH)_3.COOH$. It is obtained by the direct action of bromine on gallic acid, and forms fine white needles of bitter taste, almost insoluble in cold but readily soluble in boiling water. It is also dissolved by alcohol and ether. It is a valuable substitute for metallic bromides as a sedative in nervous complaints.

"Gallanol," or *galanilide*, $C_6H_2(OH)_3.CO.NH.C_6H_5$. This body forms white crystals melting at 205°, soluble in water, alcohol and ether. It has marked astringent properties, and being less irritant and non-poisonous, is preferred to chrysophanic acid and pyrogallol in the treatment of skin diseases.

Gallacetophenone, $C_6H_2(OH)_3.CO(CH_3)$, has already been described on page 32.

[1] According to P. Thibault (*J. S. C. I.*, 1902, p. 135), "dermatol" is not a basic salt of bismuth, but is *bismuthogallic acid*, of the formula $C_6H_2.COOH(OH)O_2.Bi(OH), H_2O$.

Pyrogallol. Pyrogallic Acid. $C_6H_6O_3$; *i. e.*, $C_6H_3\begin{cases}OH^{(1)}\\OH^{(2)}\\OH^{(3)}\end{cases}$

Pyrogallol has the constitution of a trihydroxy-benzene, and hence is isomeric with phloroglucol and hydroxy-quinol. Thus:—

	Pyrogallol.	Phloroglucol.	Hydroxyquinol.
Position of OH-groups in benzene-ring	1 : 2 : 3	1 : 3 : 5	1 : 2 : 4
Melting point, ° C.	131°	218°	140.5°
Coloration with ferric chloride	Red.	Dark violet.	Greenish-brown.

Phloroglucol is described in Vol. III, Part ii. Hydroxyquinol has no practical interest.

Pyrogallol is produced when carbon dioxide is split off from gallic acid or from the isomeric pyrogallol-carboxylic acid, in both of which bodies the three hydroxyl-groups occupy consecutive positions in the benzene-nucleus. Pyrogallol is formed when the above-named acids are heated alone, as was first observed by Scheele (1786), but better by heating with water to 210°. It may also be prepared by heating a solution of commercial gallotannic acid in glycerin to 200°, diluting with water, and extracting the pyrogallol by agitation with ether.

Pyrogallol may be conveniently obtained by mixing gallic acid with twice its weight of aniline. The mixture at first becomes liquid, and then suddenly solidifies with rise of temperature. On heating the product to 120° till carbon dioxide is no longer evolved, *aniline pyrogallate* separates out on cooling in long needles, melting at 55° to 56°. On treating this compound with cold benzene, pure aniline is dissolved, and pyrogallol remains insoluble. Several organic bases besides aniline effect the same result, but pyridine does not react until heated considerably above its boiling-point.

Pyrogallol can also be prepared by fusing either of the two parachlorphenol-disulphonic acids with potash, and it results from the action of fused caustic alkali on hæmatoxylin.

Pyrogallol forms white leaflets or thin lustrous needles, having a specific gravity of 1.463. It melts at 131° to 132° (not at 115° to 118° as sometimes stated). When cautiously heated above this temperature, pyrogallol can be sublimed without decomposition; but when rapidly heated to 250°, it loses the elements of water and is converted into a more or less indefinite body termed *metagallic acid*, which forms a black, amorphous mass insoluble in water but soluble in alkalies.

Pyrogallol dissolves in less than three parts of cold water, to form a solution of acid and bitter taste. It is also freely soluble in alcohol and ether, but practically insoluble in absolute chloroform.

Pyrogallol forms salts with bases, but its acidic characters are not very strongly marked, and the salts are very unstable.[1] Pyrogallic acid itself is stable in the dry state, when the atmosphere is free from ammonia, but in moist or ammoniacal air it gradually darkens and turns brown. In aqueous solution this change occurs far more rapidly, and is attended with absorption of oxygen.[2] In the presence of ammonia or fixed alkali, the absorption of oxygen by pyrogallol is extremely rapid, the liquid quickly becoming brown and finally black. This behaviour of an alkaline solution of pyrogallol is employed for the determination of oxygen in air and other gaseous mixtures, but has been objected to on the ground that the absorption of oxygen is attended with simultaneous evolution of carbonic oxide.[3]

[1] *Barium pyrogallate*, $C_6H_3(OH)O_2Ba+4H_2O$, has been prepared by mixing aqueous pyrogallol with excess of baryta-water. It forms colourless needles which rapidly blacken in the air, and are decomposed when boiled with water.

[2] The oxidation of pyrogallol in acid or neutral solutions results in the formation of purpurogallol or purpurogallin, a body of the formula $C_{20}H_{16}O_9$. It is most readily obtained by treating a solution of 20 parts of pyrogallol in 330 parts of water with a solution of 87 parts of potassium ferricyanide in 330 parts of water. Gas is evolved, the solution loses its deep red colour, and purpurogallin separates, the oxidation being complete in about half an hour. Purpurogallin crystallises from alcohol in brown velvet-like needles, melting at 156°, and volatilising at 200° with partial decomposition. It dissolves with difficulty in water, but readily in alcohol and ether, and is soluble in alkalies to form unstable blue compounds. The sodium salt contains Na_4, and gives with barium chloride an almost insoluble precipitate of the barium compound. In strong sulphuric acid, purpurogallin dissolves to a liquid which gives an intense violet coloration when a trace of nitrous acid or a nitrite is added. The colour is fugitive, but the reaction is said to be delicate and characteristic. (S. C. Hooker, *Ber.*, xx, 3259.)

[3] F. Clowes (*Proc. Chem. Soc.*, 1895, p. 200) finds that when the absorption of oxygen is effected by a solution containing 10 grammes of pyrogallol and 24 of caustic potash per 100 c.c., no carbon monoxide is evolved unless the oxygen in the gaseous mixture exceeds 28 per cent., and in such cases perfectly accurate determinations of oxygen are obtainable if the carbon monoxide evolved be absorbed by cuprous chloride before taking the reading. If the proportion of caustic alkali be increased to 120 grammes per 100 c.c., no evolution of carbonic oxide occurs. The question has been further studied by M. P. E. Berthelot (*Compt. rend.*, 1898, cxxvi, 1066, 1459; abst. *Jour. Chem. Soc.*, 1898, i, 645; ii, 534), who states that in presence of 3 molecules of potassium or sodium hydroxide 1 molecule of pyrogallol absorbs 3 atoms of oxygen, the carbon monoxide evolved being 2.2 per cent. of the volume of oxygen absorbed. With 3 equivalents of barium hydroxide, however, only 1 atom of oxygen is absorbed, and less carbon monoxide is formed. With ammonia the absorption is at first very rapid, but is ultimately very slow, 4 atoms of oxygen being ultimately absorbed. No nitrates are formed, but possibly an azo-compound is produced.

According to M. P. E. Berthelot (abst. *Jour. Chem. Soc.*, 1898, i, 645), the chief products of the oxidation of pyrogallol in presence of potassium or sodium hydroxide are carbon dioxide and about 86 per cent. of a dark brown substance soluble in water having the composition $C_{20}H_{20}O_{16}$. A dark red, crystallisable body, containing $C_{20}H_{20}O_{11}$, soluble in ether and having some of the properties of purpurogallin (from which it differs by $2H_2O$), is formed in the early stages of oxidation; while another body soluble in ether, and of the probable formula $C_{16}H_{16}O_{12}$, exists in the final products in quantity equal to about 10 per cent. of the original pyrogallol.

With lime-water, or calcium chloride and ammonia, in presence of air, pyrogallol gives a fine purple coloration, rapidly changing to brown, but no precipitate is produced. The reaction is delicate and characteristic.[1]

Pyrogallol rapidly reduces salts of mercury, silver and gold, with precipitation of the metal, and formation of acetic and carbonic acids. Fehling's solution and potassium ferricyanide are also reduced, and potassium permanganate in acid solution is rapidly decolorised with evolution of carbon dioxide.

With ferrous sulphate, especially if a little ferric salt be present, pyrogallol gives a blue coloration, rapidly changing to green and red; and with ferric chloride it at once gives a red coloration, turning brown on heating the liquid.

The aqueous solution of pyrogallol is turned brown by nitrous acid. The reaction is very delicate.

Pyrogallol does not precipitate a solution of gelatin. Other reactions of pyrogallol are given on page 120.

Pyrogallol might probably be determined by titration in acid solution with standard permanganate, or perhaps by means of Fehling's solution.

Pyrogallol reacts with formic aldehyde to form a condensation-product of a deep red colour. Pyrogallol forms several well-

[1] For examining the behaviour of pyrogallic acid with lime-water, it is convenient to employ a nitrometer filled with mercury. A few cubic centimetres of the solution to be tested for pyrogallol are first allowed to enter through the tap, and the cup is rinsed with water, which is allowed to enter in its turn. Ammonia is next run in, when a slight brown coloration is usually produced owing to dissolved oxygen. On now allowing lime-water or calcium chloride to enter, a fine but rapidly fading purple colour will be developed, and this will be enormously intensified on admitting air and agitating the tube; in fact, in the entire absence of oxygen, the purple-blue colour would probably not be produced. In the absence of calcium (or barium) compounds only a brown colour is produced on admitting air. Addition of potassium ferricyanide to the ammoniacal liquid produces an immediate dark brown coloration, apparently owing to the formation of the same oxidation-product as is produced by admitting air; but ferricyanide prevents the formation of the blue colour with calcium salts, probably by immediately forming the more hihgly-oxidised brown product.

defined sulphonic acids, which form crystallisable salts (M. Delage, *Compt. rend.*, cxxxi, 450).

When fused with ammonium oxalate, pyrogallol yields *ammonium rufigallate* (see p. 118).

Pyrogallol possesses well-marked toxic properties, and a case of fatal poisoning by its ingestion is on record (*Pharm. Jour.*, 1896, ii, 260). The lethal dose is about 0.1 gramme per kilogramme of body-weight, and the symptoms are similar to those produced by phosphorus-poisoning. Pyrogallol retards the heart's action and alters the appearance of the blood (Gibbs and Hare, *Amer. Chem. Jour.*, xii, 365).

ETHERS AND ESTERS OF PYROGALLOL.

Some of the pyrogallyl esters are prepared on a small scale for medicinal purposes.

Pyrogallyl Monacetate or *Pyrogallol-dimethyl Ether*, $C_6H_3.(OH)_2(O.C_2H_3O_2)$, is known under the name of "*Eugallol.*" It is very soluble in water, but is of too irritating a nature to be used in ordinary dermatological practice. It is of a syrupy consistence and easily soluble in acetone. When a very energetic action on a limited portion of the skin is required, this body has been found very useful, as it can easily be applied as a solution in acetone, which rapidly evaporates and leaves the eugallol on the desired place. *Pyrogallol triacetate* is a white powder insoluble in water, and is known as "*Lenigallol.*" It has been very successfully employed in cases of psoriasis. The *disalicylate* is known as "saligallol," and is sometimes employed in similar cases (see page 97).

Dimethyl Pyrogallate, $C_6H_3(OH).(OCH_3)_2$, and its homologues occur in the less volatile fractions of beechwood-tar (compare Part ii). They owe their chief interest to the remarkable series of colouring-matters originally prepared from them by Runge.

By condensing pyrogallol-dimethyl ether with tiglic aldehyde, Doebner has obtained an artificial resin closely resembling the natural products. When guaiacol is condensed in conjunction with dimethyl gallate, the resin obtained is isomeric with *guaiaconic acid*, one of the constituents of guaiacum-resin. Doebner's results support the view that the natural resins are in many cases condensation-products of phenols with aldehydes.

PHTHALIC ACIDS. CARBOXYL-BENZOIC ACIDS.

$$C_8H_6O_4;\ i.\ e.,\ C_6H_4\left\{\begin{array}{l}CO.OH\\CO.OH\end{array}\right.$$

Three isomeric acids of the above constitution are known, differing from each other in their properties and sources, ac-

cording to the relative positions of the carboxyl-groups in the benzene-nucleus. Thus, on oxidation with dilute nitric acid or an alkaline solution of potassium permanganate, the three isomeric xylenes yield the corresponding phthalic acids. These may, in fact, be regarded as the final products of the limited oxidation of the great majority of benzene-derivatives containing two side-chains. Hence the differentiation of the phthalic acids affords, in this as in many other cases, a valuable means of distinguishing between allied or isomeric bodies of the aromatic series, and of studying their constitution. Thus the formation of phthalic acid by the oxidation of naphthalene affords most valuable evidence of the constitution of that hydrocarbon.

The following table exhibits the leading points of difference between the isomeric phthalic acids:—

	Orthophthalic or Ordinary Phthalic Acid.	Metaphthalic or Isophthalic Acid.	Paraphthalic or Terephthalic Acid.
Formula	$C_6H_4\begin{cases}(1)\ CO.OH\\(2)\ CO.OH\end{cases}$	$C_6H_4\begin{cases}(1)\ CO.OH\\(3)\ CO.OH\end{cases}$	$C_6H_4\begin{cases}(1)\ CO.OH\\(4)\ CO.OH\end{cases}$
Chief sources and modes of formation	Oxidation of ortho-xylene, alizarin, purpurin, benzene, naphthalene, and naphthalene dichloride.	Oxidation of meta-xylene and colophony.	Oxidation of para-xylene, turpentine oil, cymene, eucalyptus oil, etc.
Crystalline form	Monoclinic prisms or nacreous laminæ.	Slender hair-like needles.	Amorphous or crystalline powder.
Melting-point	213° when rapidly heated; with decomposition.	Above 300°.	Sublimes without melting.
Solubility in water	Cold, 1 in 180 parts; boiling, more easily soluble (1 : 6).	Cold, 1 in 7800; boiling, 1 in 460 parts.	Cold, very slight; boiling, sparingly.
" in alcohol	1 in 10 parts.	Readily.	Very slight.
" in ether	3 in 2 parts.	....	Insoluble.
Action of chromic acid mixture	Completely oxidised.	Not affected.	Not affected.
Barium salt	Small scales or silky needles, only slightly soluble in hot water.	Crystallises in readily soluble needles, containing $6H_2O$.	White granular powder or concentrically arranged tablets containing $4H_2O$, soluble in 350 parts of cold water.
Silver salt	Crystalline and moderately soluble; detonates when heated rapidly.	Amorphous precipitate; forms Pharaoh's serpents on heating.	Amorphous precipitate, blackening in the light.

Ortho-phthalic Acid.[1] $C_6H_4(COOH)^1(COOH)^2$

Ordinary phthalic acid is now manufactured on a large scale by converting naphthalene into the tetrachloride,[2] and heating this with 5 to 6 parts of nitric acid of specific gravity 1.36, till entirely dissolved, when the excess of nitric acid is expelled, and the phthalic acid crystallises out on cooling. It may be purified by re-crystallisation from hot water. The yield by this process is about 30 per cent. of the naphthalene used. Phthalic acid may also be obtained by treating naphthalene direct with nitric acid of 1.15 specific gravity, but only about 40 per cent. of the theoretical yield is obtained.

According to H. Luddens (*J. S. C. I.*, 1891, x, 758), the greater part of the phthalic acid employed in the manufacture of eosin and other phthaleïn-dyes is prepared by the direct oxidation of naphthalene by chromic acid mixture (*sodium* chromate and sulphuric acid), notwithstanding the general impression that other compounds are destroyed by this reagent.[3]

Many of the properties of phthalic acid have already been described (page 128).

According to Lossen, the melting-point of phthalic acid is 184°, while Ador states that the crystals melt at 213° and the powder at 203°. These different results depend on the rapidity with which the acid is heated, as upon melting it is converted into its *anhydride*, which melts at a considerably lower temperature than phthalic acid itself. Neither iso- nor tere-phthalic acid forms an anhydride.

Phthalic acid is readily extracted from aqueous liquids by agitation with ether or benzene, but is insoluble in chloroform (distinction from benzoic acid).

When heated to 330° with a single equivalent of lime, phthalic acid yields calcium benzoate and carbonate:—$2C_8H_6O_4 + 2CaO = Ca(C_7H_5O_2)_2 + CaCO_3 + H_2O$. When heated with a larger proportion of lime or other strong base, phthalic acid yields a carbonate and benzene:—$C_8H_6O_4 + 2CaO = 2CaCO_3 + C_6H_6$.

[1] The constitution $C_6H_4\left\{\begin{matrix}CO\text{——}\\C(OH)_2\end{matrix}\right\}O$ has been suggested for phthalic acid. This formula represents it as a *γ-dihydroxylactone*.

[2] NAPHTHALENE TETRACHLORIDE, $C_{10}H_8Cl_4$, is manufactured by grinding one part of naphthalene and two of potassium chlorate with water, making the paste into balls, and bringing these after drying into 10 parts concentrated hydrochloric acid. The product is washed with water and petroleum spirit. Another method consists in passing chlorine gas through melted naphthalene, taking care that the temperature does not exceed 160° to 170° C.

[3] Phthalic and benzoic acids may be obtained by heating α- or β-naphthol (or other naphthalene derivatives, such as nitronaphthalene, the naphthylamines, etc.) with metallic oxides or peroxides in presence of caustic alkali to a temperature of about 250° C. (*Brit. Patent*, No. 15527, 1901).

By treatment with fuming nitric acid, phthalic acid is converted into nitrophthalic acid, $C_8H_5(NO_2)O_4$, but by strong chromic acid mixture it is completely oxidised.

By treatment with zinc and acetic acid, phthalic acid is converted into phthalide, $C_8H_6O_2$, diphthalyl, $C_{16}H_8O_4$, being also formed.

When treated in warm alkaline solution with sodium amalgam, phthalic acid is reduced to *hydrophthalic acid*, $C_8H_8O_4$,[1] which crystallises in tables, dissolves easily in hot water and alcohol, melts with decomposition at about 200°, and is converted into benzoic acid by treatment with nitric acid, chromic acid, or bromine-water.

When distilled with aniline, phthalic acid is converted into phenyl-phthalimide or *phthalanil*, $(C_8H_4O_2)N.C_6H_5$, a body crystallising from alcohol in needles melting at 205°, but volatile at a lower temperature. Phthalanil has been recommended as a febrifuge.

Besides the extensive employment of its anhydride in the production of eosin dyes, phthalic acid itself has found valuable application as a reagent for separating certain of the alcoholic constituents of essential oils in a state of purity. Thus the acid phthalates of these bodies are readily prepared and may be differentiated by their solubilities and other characters.

By the prolonged heating of a mixture of glycerin with phthalic anhydride or phthalic acid, and distilling the product *in vacuo*, Watson Smith (*J. S. C. I.*, 1901, p. 1075) obtained *diglyceryl triphthalate* as a transparent vitreous solid, which softens on heating and may be employed as a cement for glass and porcelain. It is insoluble in almost all solvents, but dissolves to a slight extent in glycerin and acetone.

On heating glyceryl phthalate with resorcinol, *fluoresceïn* is formed. This reaction is a useful test for the presence of combined phthalic acid.

Phthalic Anhydride. Phthalic Oxide.

$$C_8H_4O_3;\ i.\,e.,\ C_6H_4:\left\{\begin{matrix}(^1)CO\\(^2)CO\end{matrix}\right\}O$$

Phthalic anhydride is prepared by heating phthalic acid to about 200° in a current of air or carbon dioxide, when the anhydride sublimes in long, white, pliant, rhombic needles. It melts at 128° and boils at 284.5° C. It is only very slightly soluble in cold but more readily in hot water, and is reconverted

[1] Meta- and para-phthalic acids are not reduced by sodium amalgam in the cold, but on heating they both yield tetrahydro-acids, $C_8H_{10}O_4$, no intermediate product being formed (*Jour. Chem. Soc.*, lii, 370).

into phthalic acid by prolonged boiling with water, and more readily in the presence of alkalies.

Phthalic anhydride is manufactured extensively for the preparation of the class of colouring-matters known as *phthaleïns*, of which the various eosins and rhodamine are examples.

Phthaleïns.

The phthaleïns are compounds produced by the action of phthalic acid or anhydride on phenols, with elimination of water. Thus, at a moderate temperature, two molecules of ordinary phenol react with one of phthalic acid or anhydride, to form *phenol-phthaleïn*:—

$$C_6H_4\begin{cases}CO.OH\\CO.OH\end{cases} + 2C_6H_4(H).OH = C_6H_4\begin{cases}CO.C_6H_4.OH\\CO.C_6H_4.OH\end{cases} + 2H_2O$$

At a higher temperature, by the reaction of one molecule of each body, oxyanthraquinone, a derivative of anthracene, is formed:—

$$C_6H_4\begin{cases}CO.OH\\CO.OH\end{cases} + C_6H_5.OH = C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}C_6H_3OH + 2H_2O$$

Similarly, when resorcinol, $C_6H_4(OH)_2$, is heated with excess of phthalic anhydride to about 200° C. for half an hour, the mixture acquires a yellowish red colour, and contains *fluoresceïn*, $C_{20}H_{10}O_5$, the anhydride of *resorcinol-phthaleïn*. The melt dissolves in dilute caustic soda or ammonia with dark red colour, the solution changing on dilution to reddish-yellow and yellow, and exhibiting after dilution a fine yellowish-green fluorescence, which is visible in solutions so weak as to appear colourless by transmitted light. On acidulating the solution and agitating with ether, the fluoresceïn is taken up, and will be again dissolved on agitating the ethereal solution with caustic soda. If phloroglucol be substituted for resorcinol a yellow liquid is obtained, while pyrogallol yields a blue; but neither is fluorescent. The blue colour due to pyrogallol may be destroyed by cautious addition of permanganate, which acts only slowly on fluoresceïn. *Catechol-phthaleïn*, formed by gently heating catechol with phthalic anhydride and a little sulphuric acid, dissolves in caustic alkali solution with fine blue colour. *Quinol-phthaleïn*, or *quinizarin*, formed in a similar manner, dissolves in alkalies with violet-blue colour. If the solution be acidulated with sulphuric acid, it becomes red, and the quinizarin may be extracted by agitation with ether, and recovered from the ethereal liquid by shaking with caustic soda solution, which acquires a violet-blue colour.

As a class, the phthaleïns are weak acid bodies, nearly insoluble in water, but soluble in alcohol and readily so in ether. Their salts with the alkali-metals are soluble and strongly coloured. By the action of nascent hydrogen, the phthaleïns assimilate

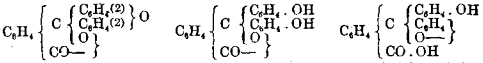
H_2 and are converted into the corresponding *phthalins*, which are colourless bodies absorbing oxygen from the air with reformation of phthaleïns. The phthaleïns of phenol, resorcinol, and pyrogallol are the most important.

The following phthaleïns are among those of greatest practical interest. Phenol-phthaleïn, galleïn and cœruleïn are described below. The eosins and other derived phthaleïns are described in detail in Vol. III, Part i.

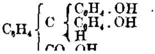
Commercial Name.	Chemical Name or Nature.	Formula.
Phenol-phthaleïn.	Phenol-phthaleïn.	$C_6H_4\left\{\begin{matrix}CO.C_6H_4(OH)\\CO.C_6H_4(OH)\end{matrix}\right.$
Resorcinol-phthaleïn	Resorcinol-phthaleïn.	$C_6H_4\left\{\begin{matrix}CO.C_6H_3(OH)_2\\CO.C_6H_3(OH)_2\end{matrix}\right.$
Fluoresceïn	Anhydride of resorcinol-phthaleïn.	$C_6H_4\left\{\begin{matrix}CO.C_6H_3(OH)\\CO.C_6H_3(OH)\end{matrix}\right\}O$
Chrysolin	Sodium salt of benzyl-fluoresceïn.	$C_6H_4\left\{\begin{matrix}CO.C_6H_3(OC_7H)_7\\CO.C_6H_3(ONa)\end{matrix}\right\}O$
Eosins	Various derivatives of fluoresceïn; *e.g.*, Cyanosin, the potassium salt of methyl-tetra-bromo-dichloro-fluoresceïn.	$C_6H_2Cl_2\left\{\begin{matrix}CO.C_6HBr_2(OCH_3)\\CO.C_6HBr_2(OK)\end{matrix}\right\}O$
Rhodamine	....	$C_6H_4\left\{\begin{matrix}CO.C_6H_3.N(C_2H_5)_2\\CO.C_6H_3.N(C_2H_5)_2\end{matrix}\right\}O$
Galleïn	Pyrogallol-phthaleïn.	$C_6H_4\left\{\begin{matrix}CO.C_6H_2(OH)_3\\CO.C_6H_2(OH)_3\end{matrix}\right.$
Cœruleïn	Anhydride of pyrogallol-phthaleïn.	$C_6H_4\left\{\begin{matrix}CO.C_6H_2(OH)_2\\CO.C_6H_2(OH)_2\end{matrix}\right\}O$

PHENOL-PHTHALEÏN. $C_{20}H_{14}O_4$; *i. e.*, $C_6H_4\left\{\begin{matrix}{}^{(1)}CO.C_6H_4(OH)^p\\{}^{(2)}CO.C_6H_4(OH)^p\end{matrix}\right.$

According to the above formula, phenolphthaleïn has the constitution of its p_2-dihydroxydiphenyl-phthalide, but the formation of phenolphthalein-oxime and some other reactions suggest the presence in free phenol-phthaleïn of the lactone ring, which in the salts is converted into a quinonoid union with a benzene-nucleus:—



Anhydride of Phenol-phthaleïn. Free Phenol-phthaleïn. Phenol-phthaleïn in its salts.



As already stated, phenolphthaleïn results from the action of phenol on phthalic acid or anhydride. For its preparation, 5 parts of phthalic anhydride, 10 of phenol, and 4 of concentrated sulphuric acid should be heated together to 120° for ten hours. The product is boiled with water, and the residue dissolved in dilute caustic soda. On filtering the liquid, the anhydride remains behind, while the phenolphthaleïn itself is precipitated on treating the filtrate with acetic acid and a little hydrochloric acid. It may be purified by dissolving in alcohol, boiling with animal charcoal, and reprecipitating by diluting the liquid with boiling water.[1]

Phenolphthaleïn usually occurs as a yellow powder, but by crystallisation from alcohol may be obtained in colourless crusts, melting at 250°. It is only slightly soluble in water, but is readily dissolved by alcohol and ether. In solutions of alkali-metal hydroxides and carbonates, it dissolves with deep red colour.

Silver nitrate gives a violet precipitate with a solution of phenolphthaleïn.

On treatment with caustic soda and zinc-dust, phenolphthaleïn assimilates two atoms of hydrogen, with reduction to *phthalin*, or *p-dihydroxy-triphenyl-methane-o-carboxylic acid*, $C_{20}H_{16}O_4$. (See page 131.) This body forms small needles melting at 225°, and is soluble in caustic alkalies without colour, but its alkaline solution is immediately turned red by adding potassium ferricyanide, owing to the formation of phenolphthaleïn.

Phenolphthaleïn is not used in dyeing. It finds some use in medicine as a laxative, in doses from 1 to 5 grains (0.05 to 0.3 gramme). Its chief interest, however, is as an indicator of neutrality, for which application it is invaluable.

The great majority of indicators of neutrality, including the colouring-matter of litmus, are bodies of acid character, and owe their value to the fact that solutions of their alkali-metal salts have a colour distinctly different from that of the free acid or hydrogen salt. When the acidic properties of the colouring matter are very feeble, as in the case of phenolphthaleïn, very weak acids will displace it from its salts, with the characteristic change of colour, indicating the liberation of the colour-acid. In solution in the free state, phenolphthalein is practically colourless, whereas its soluble metallic salts have a magnificent crimson-red colour. Hence the smallest trace of caustic alkali develops the coloration, while, on the other hand, very feeble acids destroy the colour so produced. Thus the red colour disappears when sufficient carbonic acid has been added to convert the alkaline hydroxide into acid carbonate, $MHCO_3$.

[1] **Fluorane or *o*-Phenolphthaleïn Anhydride, $C_{20}H_{12}O_3$ (see p. 132), is formed as a secondary product in the preparation of phenolphthaleïn. It melts at 173° to 175°.**

When intended for use as an indicator, phenolphthaleïn should be employed as a 1 per cent. solution in alcohol. A few drops of this reagent, which keeps perfectly, should be added to the liquid to be titrated. The alkali employed may be potassium or sodium hydroxide, but it is important that it should be free from carbonate. Hence baryta-water is to be preferred in many cases, since the insolubility of barium carbonate in water insures the freedom of the solution from that compound. The formation of an insoluble barium salt (*e. g.*, sulphate, oxalate, tartrate) in the liquid is rather an advantage than otherwise, as the pink coloration which marks the completion of the titration is observed with greater facility against the white precipitate than against white porcelain or other external background.

Ammonia is not a suitable alkali for use in conjunction with phenolphthaleïn. Owing to the formation of *phenol-di-imido-phthaleïn*, $C_{20}H_{16}N_2O_2$, a body giving a colourless solution with alkalies, the results in presence of ammonia are erratic. An approximation to the truth can be obtained by operating at as low a temperature as possible, and employing a large amount of the indicator, but the results are less satisfactory than those readily obtainable by the use of other indicators. (See J. H. Long, *Amer. Chem. Jour.*; *Analyst*, 1890, pp. 38, 52.)

With the aid of phenolphthaleïn, the great majority of acids can be accurately titrated in cold aqueous solution. The end of the reaction is well defined, especially when the titration is from acid reaction to alkaline.

Phenolphthaleïn is particularly valuable for the titration of comparatively feeble acids, the soluble normal salts of which exhibit an alkaline reaction to litmus. In the majority of cases, the point of neutrality with phenolphthaleïn is reached when sufficient alkali has been added to replace all the basic hydrogen of the acid, but in other cases the neutral point is attained when one-half or two-thirds of this amount of alkali has been added.

Such feeble acids as carbonic and sulphydric can be titrated with phenolphthaleïn, the point of neutrality in cold solutions being indicated by the formation of the compounds $NaHCO_3$ and NaHS respectively. On the other hand, aqueous solutions of silicic and boric acids are wholly indifferent to phenolphthaleïn, so that the whole of the base present as a silicate or borate is indicated on titration with a mineral acid. In presence, however, of a sufficient proportion of glycerol (not less than 30 per cent.) R. T. Thomson has made the valuable observation that boric acid can be titrated by means of phenolphthaleïn, the salt $NaBO_2$ being neutral to that indicator under these conditions.

An important advantage possessed by phenolphthaleïn is

that it reacts perfectly in alcoholic solution, and hence allows of the accurate titration of many insoluble or sparingly soluble organic acids, including benzoic, salicylic, palmitic, stearic, oleic, ricinoleic,[1] the acids of colophony, etc.

In many cases (as in the determination of benzoic acid in paregoric) phenolphthaleïn may be conveniently employed with an ethereal solution of the acid to be titrated.

Although phenol and other bodies containing an OH group have many of the properties of acids, they do not indicate this character to phenolphthaleïn. This is true of morphine, the molecule of which contains a hydroxyl-group having a phenolic function, which enables it to form compounds with the alkalies, and is the cause of its solubility in caustic alkalies and lime-water.

R. T. Thomson has investigated the general behaviour of indicators of neutrality in a very complete manner, and arranges the various indicators in three groups,[2] to which the author has added *Poirrier's soluble blue*, CLB, as a fourth, thus:—

(A) Methyl-orange Group.	(B) Litmus Group.	(C) Phenolphthaleïn Group.	(D) Poirrier's Soluble Blue.
Methyl-orange. *Cochineal.* Congo-red. Lacmoid. Iodeosin. Dimethyl-amido-azobenzene.	Litmus. *Rosolic acid.* Phenacetolin.	Phenolphthaleïn. *Turmeric.*	Soluble blue, CLB.

Broadly, the indicators of the methyl-orange group do not react with any but acids of strong affinity, but are sensitive to bases of feeble affinities, such as are many alkaloids. Litmus is often an uncertain indicator of neutrality, as the point at which the change of colour occurs does not in all cases correspond sharply with the formation of any definite salt. Phenolphthaleïn is a very delicate and sensitive indicator for the strongest as well as for most very feeble acids.

The different behaviour of various indicators has been explained by Berthelot, who has pointed out that an acid which can be accurately titrated with methyl-orange is one of which

[1] In the case of the higher fatty acids, titration in alcoholic solution is necessary not only because the acids themselves are insoluble in water, but also owing to the fact that water effects partial decomposition of their alkali-metal salts (soaps).

[2] For details of the behaviour of these various indicators, the author's paper on "Neutrality" should be consulted (*Analyst*, xvii, 186, 215; and *Pharm. Jour.* [3], xxii, 752, 772). See also G. H. A. Clowes, *Amer. J. Pharm.*, 1904, page 453.

the heat-formation exceeds 10.2 calories. Phenolphthaleïn, on the other hand, enables any acid to be titrated the heat-formation of the potassium salt of which exceeds 6 to 7 calories. With Poirrier's soluble blue still feebler acids can be titrated, but the lower limit of its applicability has not been ascertained, and its indications are in many cases disturbed by dissociation.[1]

In the table on page 137, which has been enlarged by the author from one compiled by R. T. Thomson (*J. S. C. I.*, 1887, vi, 198), the figures represent the number of atoms of basic hydrogen displaced by sodium or potassium in the form of caustic alkali, when a compound is formed having a neutral reaction to the indicator in question. Thus when methyl-orange is used in the titration of sulphurous acid, the neutral point is reached when caustic soda has been added in quantity sufficient to form the compound $NaHSO_3$; but when phenolphthaleïn is used, the point of neutrality corresponds to the salt Na_2SO_3. Similarly, NaH_2PO_4 is neutral to methyl-orange, Na_2HPO_4 to phenolphthaleïn, and Na_3PO_4 to Poirrier's blue.

While phenolphthaleïn is a delicate indicator even for feeble acids, it is absolutely indifferent to the great majority of organic bases, including even aniline and pyridine. The mydriatic alkaloids (atropine, homatropine, hyoscine, and hyoscyamine) form notable exceptions, the aqueous solutions of the free bases strongly reddening phenolphthaleïn. This property, however, does not exist in alcoholic solution, a fact which marks a curious distinction between these alkaloids and the mineral alkalies, the alcoholic solutions of which react perfectly with phenolphthaleïn. According to E. Leger, cicutine (from *Cicuta virosa*) and codeine are also exceptions to the general rule of indifference of the alkaloids to phenolphthaleïn, and P. C. Plugge states that conine and nicotine also exhibit an alkaline reaction. As a consequence of the indifference of most alkaloids to phenolphthaleïn, their salts react with this indicator as if the acids were uncombined, and hence the amount of acid in salts of aconitine, cinchonine, brucine, strychnine, morphine, quinine, quinidine, urea, etc., operating if necessary in alcoholic solution, can be ascertained by titration with standard alkali, just as if no organic base were present.[2]

[1] M. R. Engel states that about 85 per cent. of the hydrogen of H_3PO_4 and H_3AsO_4 is indicated by Poirrier's blue; while concentrated solutions of KBO_2, K_2PHO_3, K_2PHO_2, KCN, and K_2CO_3 were found to be approximately neutral. Phenol and chloral behave as monobasic acids and resorcinol as a dibasic acid, and all three can be accurately titrated with Poirrier's blue.

[2] This behaviour of alkaloids has been utilised by the author for the titration of quinidine hydriodide and cinchonidine tartrate, which salts are obtained as precipitates in the ordinary process of separating cinchona-bases (Vol. III. Part ii).

BASICITY OF ACIDS AS SHOWN BY DIFFERENT INDICATORS WHEN TITRATED IN AQUEOUS SOLUTION WITH FIXED CAUSTIC ALKALI.

ACID.		METHYL-ORANGE.	PHENOL-PHTHALEÏN.		LITMUS.		POIRRIER'S BLUE.
Name.	Formula.	Cold.	Cold.	Boiling.	Cold.	Boiling.	Cold.
Hydrochloric	HCl *	1	1	1	1	1	1
Nitric	HNO_3	1	1	1	1	1	1
Nitrous	HNO_2	Indicator destroyed	1	—	1	0	?
Sulphuric	H_2SO_4	2	2	2	2	2	2
Sulphurous	H_2SO_3	1	2	—	—	—	2
Thiosulphuric	$H_2S_2O_3$	2	2	2	2	2	—
Sulphydric	H_2S	0	1 (dilute)	0	—	0	?
Boric	H_3BO_3	0	—	—	—	—	1
Carbonic	H_2CO_3	0	1 (dilute)	0	—	0	2
Silicic	H_4SiO_4	0	—	—	—	—	?
Phosphoric	H_3PO_4	1	2	—	—	—	3 (nearly)
Arsenic	H_3AsO_4	1	2	—	—	—	3 (nearly)
Arsenious	H_3AsO_3	0	—	—	0	0	3
Chromic	H_2CrO_4	1	2	2	—	0	?
Acetic	$HC_2H_3O_2$	—	1	—	1 (nearly)	—	1
Butyric	$HC_4H_7O_2$	—	1	—	1 (nearly)	—	1
Valeric	$HC_5H_9O_2$	—	1	—	1 (nearly)	—	1
Lactic	$HC_3H_5O_3$	—	1	—	1	—	1
Oxalic	$H_2C_2O_4$	—	2	2	2	2	2
Succinic	$H_2C_4H_4O_4$	—	2	—	2 (nearly)	—	—
Tartaric	$H_2C_4H_4O_6$	—	2	—	2	—	2
Citric	$H_3C_6H_5O_7$	—	3	—	—	—	3
Carbolic (phenol)	HC_6H_5O	0	—	—	0	—	1
Picric	$HC_6H_2N_3O_7$	—	1	1	—	—	1
Benzoic	$HC_7H_5O_2$	—	1	1	1	—	1
Salicylic	$HC_7H_5O_3$	—	1	1	1 (nearly)	—	1
Hydrocyanic	HCN	0	0	—	0	—	1
Hydroferrocyanic	$H_4C_6N_6Fe$	4	4	—	4	—	—
Hydroferricyanic	$H_3C_6N_6Fe$	3	3	—	3	—	—
Thiocyanic	$HSCN$	1	1	—	1	—	1
Uric	$H_2C_5H_2N_4O_3$	0	1	1	—	—	?

* HBr, HI, and HF (probably) behave like HCl.

Until comparatively recently, the behaviour of the alkaloids with indicators had been very incompletely studied, and their titration with standard acid was rarely attempted. Where this is desired, phenolphthaleïn is quite inapplicable for their direct determination, as already stated. Litmus answers in some cases, but by no means invariably. With methyl-orange, in the majority of cases hitherto tried in the author's laboratory, determinations of tolerable accuracy and fairly sharp end-reactions are obtainable. C. Caspari (*Amer. Jour. Pharm.*, 1896, lxviii, 473) has shown that the accuracy of the results is materially affected by the presence of alcohol. The following

table shows the behaviour of various alkaloids with certain indicators. In the column headed "methyl-orange" fairly accurate titrations can be made in cases where the word *alkaline* is printed in italics. Where blanks are left, the exact behaviour of the alkaloid with the indicator is not known.

SUBSTANCE.	FORMULA.	METHYL-ORANGE.	PHENOL-PHTHALEÏN.	LITMUS.
Methylamine	CH_5N	*Alkaline*	——	Alkaline
Trimethylamine	C_3H_9N	*Alkaline*	——	Alkaline
Aniline	C_6H_7N	Alkaline	Neutral	Neutral
Pyridine	C_5H_5N	*Alkaline*	Neutral	Alkaline
Quinoline	C_9H_7N	*Alkaline*	——	——
Antipyrine	$C_{11}H_{12}N_2O$	*Alkaline*	Neutral	Neutral
Conine	$C_8H_{17}N$	*Alkaline*	Alkaline	Alkaline
Nicotine	$C_{10}H_{14}N_2$	*Alkaline*	Alkaline	Alkaline
Aconitine	$C_{33}H_{45}NO_{12}$	*Alkaline*	*Neutral*	*Alkaline*
Atropine	$C_{17}H_{23}NO_3$	*Alkaline*	Alkaline	Alkaline
Cocaine	$C_{17}H_{21}NO_4$	*Alkaline*	Neutral	Alkaline
Morphine	$C_{17}H_{19}NO_3$	*Alkaline*	Faintly acid	Alkaline
Codeine	$C_{18}H_{21}NO_3$	*Alkaline*	Alkaline	Alkaline
Strychnine	$C_{21}H_{22}N_2O_2$	*Alkaline*	Neutral	Alkaline
Brucine	$C_{33}H_{26}N_2O_4$	*Alkaline*	Neutral	Alkaline
Cinchona bases	——	Alkaline	Neutral	Alkaline
Caffeine	$C_8H_{10}N_4O_2$	Alkaline	Neutral	Neutral
Urea	CH_4N_2O	Neutral	Neutral	Neutral

In titrating quinine, the readily soluble salt represented by the formula $(C_{20}H_{24}N_2O_2)$, H_2SO_4 is neutral to methyl-orange, whereas the sparingly soluble salt containing Qu_2,H_2SO_4 is neutral to cochineal, brazil-wood, and logwood.[1] The same salt is distinctly alkaline to litmus, and hence this indicator cannot be conveniently used for the titration of quinine, though the end-reaction is well marked.

The behaviour of the alkaloids with various indicators is treated more fully in Vol. III, Part iii.[2]

Tetraiodo-phenolphthaleïn, $C_{20}H_{10}I_4O_4$, is obtained by the direct action of iodine on a solution of phenolphthaleïn. It forms a pale yellow, odourless, tasteless powder, melting at 255° with

[1] If nitric acid or hydrochloric acid be substituted for sulphuric acid, the results are similar, the salts, $Qu,2HNO_3$ and $Qu,2HCl$ being neutral to methyl-orange. These observations of the author render desirable a revision of the accepted views on the basicity of quinine.

Experiments made in the author's laboratory on the titration of cinchonine and cinchonidine with various indicators have given such anomalous results as to render it doubtful if the constitution of these bases, or at least the composition of the commercial articles, is correctly understood.

[2] See also H. W. Salomonson, *Chem. Centr.*, 1895, ii, 536, 826; abst. *Jour. Chem. Soc.*, 1896, i, 450; and C. Caspari, *Amer. Jour. Pharm.*, 1896, lxviii, 473; *Analyst*, xxi, 293.

decomposition and evolution of iodine. It is insoluble in water or alcohol, but is dissolved by ether and chloroform. It combines with alkalies to form soluble salts.

Tetraiodo-phenolphthaleïn contains 60 per cent. of iodine, which is not liberated by the action of alkalies or dilute acids, even on boiling. It is employed in medicine under the name of "*Nosophene*," and has been found valuable in skin-diseases. "*Antinosin*," the sodium salt of nosophene, is a bluish powder which is readily soluble in water, and has been found useful as an antiseptic dusting powder and internally in catarrh of the stomach and intestines.

"*Endoxine*," the bismuth salt of tetraiodo-phenolphthaleïn, is a brownish-red, odourless and tasteless powder, soluble in alkalies with bluish-violet colour. It is employed as an internal antiseptic.

GALLEÏN, $C_{20}H_{10}O_7$, is an oxidised condensation-product obtained by heating pyrogallol and phthalic anhydride to 190° to 200° C. It forms a brownish-red powder, or green crystals of metallic lustre, which are almost insoluble in water, but soluble in alcohol. Galleïn is a weak acid, forming with alkalies a blue solution which becomes dirty-coloured on standing. Galleïn dissolves in ammonia with violet colour, and the solution gives violet precipitates with metallic salts.

When heated to 200° C. with twenty times its weight of strong sulphuric acid, galleïn loses the elements of water and is converted into—

CŒRULEÏN, $C_{20}H_8O_6$, which on pouring the cooled solution into water is obtained as an amorphous black precipitate. It is nearly insoluble in water (which it colours olive-brown), alcohol, or ether, but dissolves easily in acetic acid. In commerce, cœruleïn occurs as a thick dark-coloured paste. In alkalies it dissolves with beautiful grass-green colour, and the solution gives with mordants very stable lakes. With strong sulphuric acid cœruleïn gives a dirty brown colour. On warming cœruleïn with ammonia and zinc powder, a brownish-red solution is formed, containing *cœrulïn*, $C_{20}H_{10}O_6$. The solution is oxidised on exposure to air, the original green colour being restored. Cœruleïn may be employed in dyeing in the same manner as indigo.

On treating cœruleïn-paste with two molecules of sodium bisulphite ($NaHSO_3$), a colourless compound of the two bodies is formed, which can be removed from the unaltered cœruleïn by extraction with cold alcohol. The bisulphite compound of cœruleïn occurs in commerce as a black powder under the name of *Cœruleïn S*. It dissolves in water with greenish-yellow colour, and on boiling the solution becomes deep green, and sulphurous acid is evolved. Acids and alkalies effect the same decomposition in the cold.

Cœruleïn and its bisulphite compound are used for dyeing and printing cotton fabrics, on which they produce various shades of green. The colour is not removed from the fibre by boiling soap or caustic alkalies, and is darkened by concentrated hydrochloric acid. The most characteristic reaction of cœruleïn is that with a warm acid solution of stannous chloride, which turns the fibre brownish-red owing to the formation of cœrulïn. On then washing with water, or preferably with a very dilute solution of bleaching-powder, the original green colour is restored.

RESINS.

The *Resins*[2] form a group of bodies of very complex and variable chemical constitution, but having somewhat similar physical characters.

Various substances or mixtures having the general physical characters of resins are obtainable artificially, but all the more important members of the class are natural products.

The natural resins occur, as a rule, in exudations from plants, which exudations are sometimes normal and natural, and in other cases the result of diseased conditions. The exudation of these resinous products may often be induced artificially.

The resins sometimes occur naturally in admixture with gummy matters, essential oils, etc. Resinous products which contain much gum or allied bodies—as is the case with asafœtida, galbanum, and ammoniacum—are called *Gum-resins*. Similarly, such natural products as consist of solutions or emulsions of resins in essential oils are called *Oleo-resins*, or sometimes *Balsams* or *Turpentines* (page 195).

Chemical Composition of Resins.

Even when separated from the gums, oils, and other bodies with which they frequently co-occur in nature, the resins are rarely, if ever, pure chemical compounds. They consist of a mixture of several bodies, the chemistry of which till recently was very obscure.

The resins were formerly regarded as oxidation-products of terpenes, but while this is true of some of them, it is by no means a general rule. According to the researches of Doebner, certain resins are chiefly composed of condensation-products of aromatic aldehydes and phenols; but an accurate knowledge of the chemistry of resins is chiefly due to the recent researches of A. Tschirch, who points out that the proximate constituents

[1] The Author is indebted to Mr. E. J. Parry for perusal and criticism of this section.

[2] French, *Résine;* German, *Harz.*

of resins, so far as they are known, may be classified under the following three heads:—*Resin-Esters* and their decomposition-products; *Resinolic or Resin Acids;* and *Resenes;* which last are bodies of indifferent or unknown constitution. In many of the resins one or other of these classes preponderates, and the product consequently falls into the group of *ester-resins*, *acid-resins*, or *resene-resins*. Representatives of all three classes are rarely present in the same product.

For the proximate analysis of resinous substances, Tschirch dissolves the sample in ether and agitates the solution successively with (1) a 1 per cent. solution of ammonium carbonate; (2) a 1 per cent. solution of sodium carbonate; and (3) solutions of potassium hydroxide of 0.1 and 1.0 per cent. These reagents dissolve the resin-acids, which can be precipitated from the alkaline liquids by a dilute mineral acid. On subjecting the ethereal solution to steam-distillation, any essential oil will volatilise, together with the ether. The residue may contain resin-esters and resenes, which can be separated by saponification with alcoholic potash, when the acid-radicals of the esters will form soluble potassium salts, and the resenes and resin-alcohols can be extracted by agitation with ether. The resin-alcohols can be acetylated or benzoylated, whereas the resenes resist such treatment.

Among the resins in which resin-esters predominate, Tschirch includes (1) the *benzo-resins*, gum-benzoin, Peru and Tolu balsams, storax, acaroid-resins, aloes resin, and dragon's blood; and (2) the *umbelliferous gum-resins*, ammoniacum, galbanum, sagapenum, asafœtida, and umbelliferous opopanax.

The *terpeno-resins*, consisting chiefly of resin-acids, include the various coniferous resins, copaiba balsam, and the resin of Zanzibar copal.

The resinous bodies in which *resenes* predominate include (1) the burseraceous oleo-resins, myrrh, olibanum, bdellium, burseraceous opopanax, Mecca balsam, various elemis, tacamahaca, and mastic; and (2) the dipterocarpus products, Doona resin, dammar, and Manila copal.

Resin Esters.

As a rule, the esters of the resins yield on saponification aromatic acids, such as benzoic and cinnamic acids. These resins consequently come under the denomination of *aromatic balsams*, and as such have already been described. Amber, however, contains succinic acid, which is a compound of the aliphatic series.

Benzoic acid, $C_6H_5.COOH$, occurs in Peru and Tolu balsams, Siam benzoin, and (together with benzoyl-acetic and probably phenylhydracrylic acid) in dragon's blood.

Cinnamic acid, $C_6H_5.CH:CH.COOH$, is present in Peru and Tolu balsams, storax, yellow acaroid resin, and Sumatra benzoin.

Salicylic acid, $C_6H_4(OH).COOH$, has been found in gum ammoniacum.

Para-coumaric acid, $C_6H_4(OH)^{(1)}.CH:CH.COOH^{(4)}$, is present in yellow and red acaroid resins.

Ferulic acid, $C_6H_3(OH)^{(1)}(OCH_3)^{(2)}:CH.COOH^{(4)}$, occurs in asafœtida.

Umbellic acid, $C_6H_3(H)^{(2)}(OH)^{(3)}:CH.COOH^{(4)}$, occurs, together with its anhydride *umbelliferone*, in sagapenum, galbanum, and asafœtida.

RESIN ALCOHOLS.

The alkyl-radicals of the resin-esters were practically unknown till recently, but the researches of A. Tschirch and his collaborators have resulted in the isolation of the following resin-alcohols. Tschirch distinguishes two kinds of these—*resinols* and *resinotannols*. The members of the former group are colourless and give no tannin-reaction with iron salts, while the latter are coloured and give a tannin-reaction.

RESINOLS.	OCCURRENCE.	FORMULA.	MELTING POINT, °C.	OBSERVERS.
α- and β-amyrin	Elemi.	$C_{30}H_{49}(OH)$	—	Vesterberg.
Benzoresinol	Benzoin.	$C_{16}H_{25}(OH)O$	274	Tschirch and Lüdy.
Chironol	Burseraceous opopanax.	$C_{28}H_{47}(OH)$	173 to 176	Tschirch and Baur.
Pinoresinol	Pine resin.	$C_{18}H_{18}O_6$	80 to 90	Bamberger.
Storesinol	Storax.	$C_{12}H_{20}O$ or $C_{36}H_{58}O_3$	—	von Miller.
Succinoresinol	Amber.	$C_{12}H_{20}O$	275	Tschirch and Aweng.

The table of *resinotannols* is given on page 144.

In cases where such bodies have been obtained, the products of acetylation and benzoylation of the resinotannols all contain one acetyl- or one benzoyl-group, with the exception of the product of benzoylation of aloresinotannol, which contains two benzoyl-groups in the molecule.

RESINOLIC ACIDS.

These compounds are the characteristic free acids of resins, and are in general bodies of complex constitution and high molecular weight. They usually contain one or more hydroxyl-groups as well as carboxyl-residues. Besides the many acids stated by Tschirch to exist in coniferous oleo-resins (page 200), the resin-acids tabulated on page 145 have been described.

TABLE OF RESINOTANNOLS.

Resinotannols.	Occurrence.	Formula.	Acid Product of Treatment with Nitric Acid.	Product of Fusion with Caustic Potash.	Observers.
Aloresinotannol	Cape Aloes.*	$C_{22}H_{28}O_6$.	—	—	Tschirch and Pedersen.
Ammoresinotannol	Ammoniacum.	$C_{18}H_{29}O_2(OH)$.	Styphnic acid.	Resorcinol.	Tschirch and Luz.
Asaresinotannol	Asafœtida.	$C_{24}H_{34}O_5$.	Picric acid.	—	Tschirch and Polasek.
Dracoresinotannol	Palm dragon's blood.	$C_8H_9O(OH)$; or $C_{24}H_{30}O_4$.	—	—	Tschirch and K. Dieterich.
Erythroresinotannol	Red *acaroid*.	$C_{40}H_{40}O_{10}$.	Picric acid.	—	Tschirch and Hildebrand.
Galbanoresinotannol	Galbanum.	$C_{18}H_{29}O_2(OH)$.	*Camphoric* and camphoronic acids.	—	Tschirch and Conrady.
Oporesinotannol	Umbelliferous opopanax.	$C_{12}H_{13}O_2(OH)$.	Oxalic and picric acids.	—	Tschirch and Knitl.
Panaxresinotannol	Burseraceous opopanax.	$C_{34}H_{49}O_7(OH)$.	—	—	Tschirch and Baur.
Peruresinotannol	Peruvian balsam.	$C_{18}H_{19}O_4(OH)$.	Oxalic and picric acids.	—	Tschirch and Trog.
Sagaresinotannol	Sagapenum.	$C_{24}H_{27}O_4(OH)$.	Styphnic acid.	—	Tschirch and Hohenadel.
Siaresinotannol	Siam *benzoin*.	$C_{12}H_{13}O_2(OH)$.	Picric acid.	—	Tschirch and Lüdy.
Sumaresinotannol	Sumatra benzoin.	$C_{48}H_{19}O_3(OH)$.	Picric acid.	Protocatechuic acid.	Tschirch and Lüdy.
Toluresinotannol	Tolu balsam.	$C_{17}H_{17}O_4(OH)$.	Oxalic and picric acids.	Protocatechuic acid.	Tschirch and Oberländer.
Xanthoresinotannol	Yellow acaroid.	$C_{43}H_{46}O_{10}$.	Picric acid.	—	Tschirch and Hildebrand.

* Tschirch and Klaveness (*Arch. Pharm.*, ccxxxix, p. 241; abst. *Analyst*, 1901, p. 298) have recently examined the resinotannol of Uganda aloes, the resin of which is a compound of paracoumaric acid with *Uganda-resinotannol*, $C_{22}H_{22}O_8$. This resinotannol is identical with that of Natal aloes.

TABLE OF RESINOLIC ACIDS.

Resin Acids.	Occurrence.	Formula.	Melting Point, °C.	Observers.
Agaric	......	$C_{16}H_{30}O_5 + H_2O$.	138 to 139	Jahns.
Aleuritic	Shellac.	$(C_{13}H_{20}O_4)_n$.	101.5	Tschirch and Farner.
Callitrolic	Sandarac.	{ $C_{64}H_{82}O_5(OH).(COOH)$. { $C_{30}H_{46}O_5$.	248 —	Tschirch and Balzer. T. A. Henry.
Copaivic*	Copaiba balsam.	$C_{20}H_{30}O_2$.	—	Schweitzer.
Dammarolic	Dammar.	$C_{54}H_{77}O_3(OH).(COOH)_2$.	—	Tschirch and Glimmann.
Guaiacic	Guaiacum.	$C_{20}H_{24}O_4$.	75 to 80	Döbner and Lücker.
Guaiaconic	Guaiacum.	$C_{20}H_{24}O_5$.	95 to 100	Döbner and Lücker.
Illuric	African copaiba.	$C_{20}H_{28}O_3$.	128	Tschirch.
Pimaric (inactive)	Sandarac.	$C_{20}H_{30}O_2$.	171	T. A. Henry.
Podocarpic	Podocarpin resin.	$C_{17}H_{22}O_3$.	187 to 188	Oudemans.
Sandaracolic	Sandarac.	$C_{43}H_{61}O_3(OCH_3)(OH)(COOH)$.	140 (152)	Tschirch and Balzer.
Succinoabietic	Amber.	$C_{80}H_{120}O_5$.	148	Tschirch and Aweng.
Trachylolic	Zanzibar copal.	$C_{56}H_{88}O_8$.	165	Tschirch and Stephan.
Iso-trachylolic	Zanzibar copal.	$C_{56}H_{88}O_8$.	105 to 107	Tschirch and Stephan.
Elemic	Elemi.	$C_{35}H_{46}O_4$.	—	Flückiger.
Boswellic	Olibanum.	$C_{32}H_{52}O_4$.	142 to 150	Tschirch and Halbey.
Chironolic	Burseraceous opopanax.	$C_{28}H_{48}O_4$.	100 to 108	Tschirch and Baur.
α-Masticic	Mastic.	$C_{23}H_{36}O_4$.	90 to 91	Tschirch and Reutter.
β-Masticic	Mastic.	$C_{23}H_{36}O_4$.	89.5 to 90.5	Tschirch and Reutter.
Masticolic	Mastic.	$C_{23}H_{36}O_4$.	201	Tschirch and Reutter.
α-Masticonic	Mastic.	$C_{32}H_{48}O_4$.	96 to 96.5	Tschirch and Reutter.
β-Masticonic	Mastic.	$C_{32}H_{48}O_4$.	91 to 92	Tschirch and Reutter.

* Meta- and oxy-copaivic acids, and probably also several isomeric copaivic acids, are said to occur in the different varieties of copaiba.

Certain relations, more or less fanciful, can be traced between some of the resin-acids, by consideration of their reputed formulæ, which, however, must not, in most cases, be regarded as positively ascertained. Accepting Mauch's formula for abietic acid, $C_{19}H_{28}O_2$, then pimaric acid and the copaivic acids have the composition of next higher homologues.

None of the resin-acids appear to contain more than one hydroxyl-group; but while sandaracolic and podocarpic acids contain only one carboxyl-group, two such groups appear to exist in the molecules of abietic, succino-abietic, trachylolic, and dammarolic acids.

Resenes.

These bodies are practically unclassifiable. They are oxygenated compounds, but are not acted on by alkalies and possess no characteristic chemical properties. They do not appear to be alcohols, esters, acids, ketones, or aldehydes. They are insoluble in and unacted on by caustic alkalies, a fact which gives the resins containing them one of their chief values for the manufacture of varnishes. The following are among the resenes which have been described by Tschirch and his co-workers:—

Resene.	Occurrence.	Formula.	Melting Point, °C.	Observers.
Alban	Gutta-percha.	(?) $C_{40}H_{64}O_3$.	195	Tschirch and Oesterle.
α-Copalresene	Copal.	(?) $C_{25}H_{38}O_4$.	75 to 77	Tschirch and Stephan.
β-Copalresene	Copal.	$C_{25}H_{38}O_4$.	—	Tschirch and Stephan.
α-Dammarresene	Dammar.	(?) $C_{33}H_{52}O_3$.	65	Tschirch and Glimmann.
β-Dammarresene	Dammar.	$C_{31}H_{52}O$.	206	Tschirch and Glimmann.
Dracoalban	Palm Dragon's blood.	$C_{20}H_{40}O_4$.	—	Tschirch and K. Dieterich.
Dracoresene	Palm Dragon's blood.	(?) $C_{26}H_{44}O_2$.	74	Tschirch and K. Dieterich.
Fluavil	Gutta-percha.	(?) $C_{40}H_{64}O_4$.	—	Tschirch and Oesterle.
Gurjunresene	Gurjun balsam	$C_{17}H_{28}O_2$.	—	Tschirch and Weil.
Myroxoresene	Fruit of myroxylons.	$C_7H_{10}O$.	—	Tschirch and Germann.
α-Masticoresene	Mastic.	$C_{35}H_{56}O_4$.	74 to 75	Tschirch and Reutter
β-Masticoresene	Mastic.	—	—	Tschirch and Reutter.
Olibanoresene	Olibanum.	$(C_{14}H_{22}O)_n$.	62	Tschirch and Halbey.
α-Panaxresene	Burseraceous opopanax.	$C_{32}H_{54}O_4$.	—	Tschirch and Baur.
β-Panaxresene	Burseraceous opopanax.	$C_{27}H_{42}O_5$.	—	Tschirch and Baur.

General Characters of Resins.

The resins as a class are solid, more or less transparent, brittle bodies, and in some cases are capable of crystallising. They have usually no marked odour or taste, and vary in specific gravity from 0.90 to 1.25. The resins are easily fusible, but not volatile, and are decomposed when heated in close vessels, yielding empyreumatic products consisting chiefly of hydrocarbons. Heated in the air, the resins inflame readily, and burn with a smoky flame. They are very bad conductors of electricity, and when rubbed become negatively electrified.

The resins are insoluble in water, but are soluble to a great extent in alcohol and many other organic solvents. In most cases the solutions are acid, to an extent depending on the nature of the resin, and when treated with an alkali yield a lather. The solutions of the resins in alkalies differ from ordinary soap solutions in the fact that they cannot be "salted out" by the addition of common salt, unless this be used in very large quantity.

Commercial Resins.

Many of the resins are important articles of commerce. A number of them are used to an enormous extent for the manufacture of varnishes, and in certain branches of soap-making. They are also employed for the manufacture of sealing-wax, for hat-stiffening, for incense, and to a certain extent in medicine.

In the examination of resins, the following general principles should be observed. Frequently it is not necessary to examine a resin in so full a manner as the following processes involve, but in many cases nothing but a full examination will give reliable information as to the purity of the product.

Water and certain *general impurities* may be separated from the resins by dissolving them in oil of turpentine, or other suitable solvent. If the operation be conducted in a graduated tube, the separated water may be measured and the insoluble matter filtered off, washed with the solvent, dried, weighed, and further examined. The residue thus obtained will often, especially in the case of medicinal resins, be found to consist of woody fibre.

From the *neutral fixed oils* resins may be separated by treating the mixture with alcohol of about 0.85 specific gravity. The alcohol is subsequently separated, and the dissolved resin recovered by evaporating it to dryness. The results are only approximately correct. Acid resins, such as common colophony, may be separated from the neutral fats by boiling the substance with a strong solution of sodium bicarbonate or borax. After cooling, the aqueous liquid is separated from the oil, and the resin precipitated from its solution by adding hydrochloric acid.

Methods of separating resin from fatty acids are described under "Colophony."

Resins may be separated from the *essential oils* and *camphors*, in admixture with which they so frequently occur, by distilling the substance in a current of steam, and then, if necessary, immersing the flask or retort in a calcium chloride bath, while still continuing the current of steam.

Essential oils and camphors may also be separated by rubbing down the resinous substance to a fine powder in admixture with a known quantity of sand, and then macerating in petroleum-spirit. Part of the true resin will also be dissolved, and hence the filtered solution must be evaporated to dryness, the residue heated to 110° or 120° C. till constant in weight, and the weight found added to that of the undissolved portion, when the loss will be the essential oil and other volatile constituents. The amount of resin dissolved by the petroleum-spirit is often of interest. Thus, in the case of copal, the quality of the sample is better, the smaller the quantity of non-volatile matter dissolved by the petroleum-spirit. The mixture of ethereal oil and resin left on evaporating the petroleum-spirit at the ordinary temperature often yields more or less characteristic colour-reactions with the reagents for essential oils.

The residue insoluble in petroleum-spirit should be weighed and then treated with ether, after which it should be ascertained if alcohol will extract anything insoluble in ether or petroleum-spirit. In the case of gum-resins, *sugar* is one of the principal substances extracted by alcohol, while gum, salts, etc., may subsequently be dissolved out by water, which in some cases (*e. g.*, gum tragacanth) may produce swelling without actual solution of the gummy matter. The ethereal solution should be tested as to its miscibility with alcohol, and a portion may be evaporated to dryness and the residue examined by colour-tests. It is also desirable to ascertain if a turbidity is produced by adding ether, ammonia, or an alcoholic solution of lead acetate to the spirituous solution of the original resin.

Mauch recommends the treatment of the substance with about 15 times its weight of a 60 per cent. solution of chloral hydrate in water. The liquor is filtered from woody fibre or other insoluble matter and the filtrate mixed with 10 parts of alcohol of 95 per cent. This precipitates the gummy matters in a convenient condition for filtration and weighing, while the resinous matters and essential oils remain in solution.

Useful information may also be obtained by treating the original resin with chloroform, ether, or a saturated aqueous solution of sodium carbonate, which last may produce colourations or dissolve out cinnamic acid and acid resins.

Various observers have applied to resins the methods which

have been found so valuable in the examination of fatty and essential oils. Thus the amount of caustic alkali required (1) for the neutralisation of the free acid of the resin; (2) for the saponification or hydrolysis of the esters, lactones, or anhydrides present; (3) the sum of 1 and 2; and (4) the bromine and iodine absorptions, have all been recorded. The following table shows the figures recorded by Rowland Williams (R. W., *Chem. News*, lviii (1888), page 224); A. Kremel (K., *Pharm. Jour.*, xvii (1887), page 546); E. Dieterich and K. Dieterich (E. D., K. D., *Pharm. Jour.*, xvii (1887), page 546); von Schmidt and Erban (S. and E., *J. S. C. I.*, viii (1889), page 308) and others.[1]

The acid and ester numbers in the table (p. 150) represent the numbers of milligrammes of KOH absorbed by one gramme of the sample, and were obtained in the usual manner,[2] except in the case of the gum-resins, when the titration was effected in the following way (A. Kremel; E. and K. Dieterich):—

One gramme of the gum-resin was mixed with powdered gypsum and extracted with 95 per cent. alcohol. The residue from the evaporation of the alcoholic extract (which gives the percentage of resin) was then redissolved in 50 c.c. of alcohol, one-half of the liquid being used for the acid determination and the other half for the esters. The amount of potash used was then calculated to 1 gramme of the pure resin. The method followed by von Schmidt and Erban for the determination of the amount of iodine absorbed was to dissolve 1 gramme of the resin in hot alcohol, when, after cooling the liquid, the iodine solution was added in excess. The mixture was allowed to stand for twenty-four hours before titration. The figures in the table marked with an asterisk were obtained on that portion of the resin soluble in alcohol, the insoluble matter being separated. The remaining iodine-absorption figures of von Schmidt and Erban (not marked by an asterisk) were obtained on the alcoholic solution in presence of the insoluble residue.

[1] The figures for *shellac* have been omitted from the table, since most of the samples examined were obviously adulterated. All the reliable data with reference to this resin will be found on pages 190 *et seq.*

[2] K. Dieterich has proposed a series of somewhat empirical methods of estimating the action of alkali on many of the resins. By the acid number (direct) he understands the usual figure obtained by the direct titration of the resin in a suitable solvent such as alcohol or chloroform. For resins free or nearly free from esters he proposes to employ an "indirect" acid number, obtained by allowing the resin to stand for twenty-four hours with excess of alkali, and titrating the residual alkali with standard acid. Such treatment can scarcely be regarded as determining the true acid number, as the action of the alkali may be of a very different nature from a mere combination with the acid. He also uses "hot," "cold," and "fractional" saponification, but the figures obtained appear only to complicate the subject and the advantage is on the side of the ordinary figures obtained in the usual manner.

ANALYTICAL CONSTANTS OF RESINS.

Substance.	Source or Variety.	Acid Number.	Ester Number.	Iodine Absorption.	Ash.	Observers.
				Per Cent.	Per Cent.	
Resins:—						
Amber	*Pinites Succinifer.*	15	71	62.1	0.28	R. W.
		33; 34	74; 91	...	...	K.
Anime	Various.	18 to 27	47 to 62	128 to 137	0.05 to 0.11	R. W.
Caoutchouc	... ...	81	...	71	...	S. & E.
Colophony	Residue from turpentine distillations, *Pinus* species.	146	22	116.8*	...	S. & E.
	Refined.	179; 178	8; 18	115.3; 114.8	0.05; 0.02	R. W.
	Ordinary.	169; 167	7; 23	112.0; 113.3	0.08; 1.20	R. W.
	Various.	151 to 173	...	...	...	...
Copal	*Trachylobium* and *Hymenæa* species.	30; 94	25; 89	34.8; 44.9	...	S. & E.
	Various.	80 to 147	...	...	...	...
	Various.	46 to 141	35 to 85	122 to 142	trace to 2.06	R. W.
	Various.	59 to 148	...	...	...	Lippert and Reissiger.
Copal (Kauri)	*Dammara Australis.*	52 to 63	26 to 36	151 to 164	0.08 to 0.12	R. W.
Dammar	*Dammara* and *Hopea* species.	33	14	63.6	...	S. & E.
		21 to 27	4 to 20	130 to 142	0.03 to 0.07	R. W.
	Batavia.	22	14	117.7	0.01	R. W.
	Various.	15 to 34	...	...	...	K.
Dragon's Blood	*Dæmonorops Draco*	11	142	98.4	3.58	R. W.
	and *Dracæna Cinnabari.*	...	...	72.4	...	S. & E.
Elemi	*Bursera* species.	22	3	85.1*	...	S. & E.
		16; 18	13; 8	175.4	0.04	R. W.; K.
	Manila.	3	24	...	...	K.
Guaiacum	*Guaiacum officinale.*	23 to 44	...	...	...	K.
Jalap	*Ipomœa purga.*	12; 13	120; 121	...	...	K.
Jalapin	Jalap resin.	15	173	...	...	K.
Mastic	*Pistacia lentiscus.*	50 to 56	23	159	0.14 to 0.20	R. W.
		62; 71	...	...	...	K.
		64	29	64.4	...	S. & E.

Sandarac	*Callitris quadrivalvis.*	146 to 154	1 to 11	134.3	0.04 to 0.17	R. W.
		141	33	66.8*	...	S. & E.
OLEO-RESINS[1]:—						
Canada balsam	*Abies balsamea.*	81 to 87	...	...	...	K.; E. D.
		...	4.5 to 9.0	...	...	F. Dietze.
Copaiba balsam	(See table on page 204.)					
Gurjun balsam		5.8 to 20	11.3 to 11.2	...	...	K.; E. D.
Mecca balsam	*Balsamodendron gileadense.*	40 to 52	101.4	...	...	K.; E. D.
Common turpentine.	*Pinus Sylvestris, P. Cembra, Abies* species, etc.	108 to 145	3 to 60.2	...	...	K.; E. D.
Chian Turpentine	...	48; 53	19 to 21.50	...	...	K.; E. D.
Venice Turpentine	...	68; 70	...	...	...	E. D.
		70	32	145.3*	...	S. & E.
Burgundy Pitch	...	142	...	...	...	K.
GUM-RESINS:—						
Ammoniacum	*Dorema Ammoniacum.*					
	African	59	123	...	...	K.
	Persian	57 to 135	31 to 98	...	...	K.; E. D.
Asafœtida	*Ferula* species.	11 to 82	82 to 182	...	...	K.; E. D.
Bdellium	Various *Burseraceæ.*	10 to 37	47 to 96	...	...	K. D.
Euphorbium	*Euphorbia resinifera.*	13 to 25	49 to 68	...	...	Beckurts & Brüche; K.
Galbanum	*Peucedanum* species.	5 to 69	55 to 179	...	...	E. D.
Gamboge	*Garcinia Morella.*	81	67	115.8	0.48	R. W.
		100	57	...	...	K.
Myrrh	Herabol-Myrrh.	64 to 70	95 to 146	...	...	K.
		25	204	...	...	K. D.
	Indian.	42	131	...	...	K.
Olibanum	*Boswellia* species.	45 to 88	7 to 72	...	...	K.; E. D.
	Indian.	50	60	...	...	K.

[1] Whilst retaining the ordinary names for certain oleo-resins, it may be again pointed out that these substances here treated are not true balsams, these bodies having been already discussed under the aromatic acids, since their chief characteristic *is* the presence of the acids with resinous substances.

The figures in the table on page 153, obtained by the analysis of resins used in the manufacture of spirit-varnishes, are due to A. Rudling (*J. S. C. I.*, 1903, xxii, 428). Those referring to shellac are omitted owing to the obvious impurity of some of the samples examined. The figures in columns A were yielded by the crude resins; in B by the anhydrous samples after being freed from mechanical impurities. Columns C refer to the alcoholic extract after drying at 100° C.[1]

The table on page 154 gives the results obtained by G. Gregor (abst. *Analyst*, xxiii, 318) and by Bamberger in the determination of the methoxyl-number of various resins and balsams. Gregor's modification of Zeisel's method was employed in each case (*Analyst*, xxiii. 297).

The acetyl number of resins (having the same significance as in the analysis of fatty oils) has occasionally been determined, as have the carbonyl numbers, but these figures appear to have only a limited value analytically.

The foregoing methods afford valuable indications of the nature of resinous substances, but the positive identification of the various individual resins of commerce is a matter of considerable difficulty even when only one is present, and in admixture the task is often insuperable.

This conclusion is emphasised by the fact that in the manufacture of varnishes, the resins are usually heated together with oil or other substances to a temperature of about 300° C. The effect of such heating is exemplified by various figures given by J. Lewkowitsch (*Analyst*, 1901, xxvi, p. 38). From his results it appears that not only do different commercial samples of presumably similar nature and origin give very varying figures, but the effect of heat on a given sample is often such as to destroy any analytical characters it previously possessed. It is desirable to place the results on record, but it is evident that at present any conclusion as to the origin or purity of a resin, from the figures obtained by its analysis, must be drawn with the greatest caution.

[1] In these analyses, the iodine-value was determined by dissolving 0.5 to 1.0 gramme in 25 c.c. of alcohol with 10 c.c. of chloroform, and titrating after six hours. The saponification value was determined by boiling 1 gramme of the resin for fifteen minutes with 25 c.c. of semi-normal potassium hydroxide solution under a reflux-condenser, then diluting the liquid with 100 c.c. of alcohol, and titrating with standard acid; and the acid value by boiling 1 gramme of resin for five minutes under a reflux-condenser with 100 c.c. of 96 per cent. alcohol, and titrating the liquid when cold.

ANALYTICAL CONSTANTS OF RESINS (A. Rudling).

Resin	Water.	Substance Insoluble in Alcohol.	Iodine Value.			Saponification Value.			Acid Value.		
			A	B	C	A	D	C	A	B	C
	Per Cent.	Per Cent.									
Yellow *acaroid* (xanthorrhea) resin	5.65	0.93	176.2	188.6	160.0	98.0	104.9	106.0	82.3	88.1	64.0
Yellow acaroid resin (Adelaide)	4.50	3.52	176.2	191.5	160.0	100.8	109.5	106.0	67.2	73.0	67.0
Yellow acaroid resin (Victoria)	4.40	0.88	175.0	184.7	160.0	156.8	165.5	176.4	72.8	76.8	84.0
Red acaroid resin	4.90	5.26	164.5	183.1	156.7	64.4	71.7	106.0	18.5	20.6	25.0
Sandarac	2.00	0.54	91.8	94.2	98.7	152.4	166.7	170.8	137.2	140.8	137.8
Manila (spirit soluble)	2.10	2.30	106.0	110.8	91.0	187.6	196.2	187.6	136.6	142.8	150.0
Manila (hard)	1.68	3.39	86.0	90.6	..	215.6	227.1	..	138.9	146.3	..
White French resin	0.80	0.10	137.1	138.3	..	177.8	179.4	..	169.7	171.2	..
American resin	0.75	0.20	122.0	123.2	..	182.0	183.8	..	157.9	159.4	..
Venetian turpentine (genuine)	..	..	148.5	..	..	121.8	..	..	73.9	..	..
Venetian turpentine (spurious)	..	..	109.6	..	..	117.6	..	..	103.0	..	..
Elemi	0.2	0.1	83.6	83.8	..	28.0	28.0	..	22.4	22.4	..

No.	Description of Resin or Balsam.	Methoxyl-Number.			
		Gregor.		Bamberger.	
1.	Aloë hepatica	4.2	..	3.9	
2.	Aloë lucida	0	..	0	
3.	Ammoniacum	8.6	..	11	
4.		9		—	
5.	Asafœtida	11.9	..	18	
6.		6.9		—	
7.	Gum benzoin, Siam	43.4	4.3	30	28.5
8.	Gum benzoin, Sumatra	25.5	25.3	16.5	16.2
9.		20.3		—	
10.		20.1		—	
11.	Benzoin (almond), Sumatra	20	..	13.3	
12.	Canada balsam	0	..	0	
13.	Copaiba balsam	0	..	0	
14.	Copal	0	..	0	
15.	Colophony	0	..	0	
16.	Dammar	0	..	0	
17.	Dragon's blood	27.6	..	33.8	
18.		25.3		—	
19.	Euphorbium	0	..	0	
20.		2.8		0	
21.	Elemi	0	..	0	
22.		2.5		—	
23.	Pine resin	0	..	0	
24.	Galbanum	3.7	..	3.7	4
25.	Gamboge	0	..	0	
26.		2.4		—	
27.	Guaiacum	73.8	74.2	83.8	84.0
28.	Gurjun balsam	0	..	—	
29.	Jalap resin	0	..	0	
30.	Labdanum	0	..	0	
31.	Liquidambar styrax	4.5	..	0	
32.		3.6		—	
33.	Myrrh	13.5	..	13.6	13.2
34.	Gum mastic	0	..	0	
35.		1.9		—	
36.	Olibanum	6.4	..	5.3	
37.	Balsam of Peru	16.7	..	14.4	
38.		21.8	21.7	—	
39.		22.6		—	
40.	Scammonium	0	..	0	
41.	Sandarac	0	..	0	
42.	Venice turpentine	0	..	0	
43.	Balsam of Tolu	41.6	..	46.8	
44.		41.7		—	

RESINS.

Acaroid Resins.

Red and yellow acaroid resins are the products of various species of *Xanthorrhœa*, especially of *X. australis*, plants found over a wide area of the Australian Continent. Both varieties of the resin are employed in Germany in the preparation of spirit lacquers for coating metals, especially the brass parts of scientific instruments, while the potash and soda solutions of the resins are used for sizing paper.

Red acaroid resin, the so-called "grass-tree gum," occurs in small dark red pieces containing from 5 to 10 per cent. of impurities, and differs from yellow acaroid, or "Botany Bay gum," in not giving a cinnamic acid reaction. According to Maiden, only about 2 per cent. of the yellow acaroid resin is soluble in petroleum-ether and as much as 90 to 95 per cent. in alcohol. Red acaroid resin, however, yields as much as 3 per cent. to petroleum-ether.

According to K. Hildebrand, the composition of red and yellow acaroid resins is very similar, the main distinction being the presence of cinnamic acid in the latter kind. In the red resin, which is chiefly the product of *X. Australis*, he found 1 per cent. of free *para-coumaric acid*, and 2 per cent. of this acid as an ester of *erythro-resinotannol*, $C_{40}H_{39}O_9.OH$; traces of benzoic acid also in combination; and traces of para-oxybenzaldehyde. About 85 per cent. of the resin consists of the above-mentioned compound of para-coumaric acid with the resin-alcohol.

Yellow acaroid resin contains about four per cent. of free para-coumaric acid and a small quantity of free cinnamic acid. Both acids, chiefly the former, are present in the form of esters of *xanthoresinotannol*, $C_{43}H_{45}O_9.OH$, which bodies form the principal portion of the resin. In addition to these esters, traces of several bodies which have not been definitely identified are also present. These probably consist of styracin, phenyl-propyl cinnamate, para-oxybenzaldehyde, and vanillin. Schimmel & Co. give 4.9 as the acid-number and 69.4 as the ester-number of a sample of the yellow resin. An essential oil distilled from the yellow acaroid resin, obtained from *X. hastile*, was an oil of storax-like odour, having a specific gravity of 0.937, and an optical rotation of —3.25. The saponification-number of the oil was 74.3 and the acid-number 4.9, showing the presence of a large proportion of esters. The free acid was identified as cinnamic acid, which was also found in the esters. From the low-boiling fractions of the oil, styrene was isolated.

Amber.

Amber is a fossil resin derived from *Pinites succinifer*, and a number of varieties are recognised commercially.

SUCCINITE forms yellow or yellowish-brown masses, which are often quite transparent or semi-transparent, but sometimes so milky as to be quite opaque. It is hard and brittle, and melts at about 250° to 300° C. Succinite has a specific gravity of about 1.050 to 1.096. It is used to a considerable extent for ornamental purposes, and where expense is not an object, for the very highest-class varnish.

GEDANITE, also known as "soft amber," is a pure yellow, transparent variety of amber, which swells at 140° to 180°, and melts on further heating. It is said to contain less succinic acid than ordinary amber. GLESSITE is usually brown and opaque. STANTIENITE is known as black resin and is extremely brittle. BECKERITE, or brown resin, is opaque.

According to Tschirch and Aweng, amber contains 2 per cent. of the bornyl ester of succino-abietic acid; 28 per cent. of free succino-abietic acid,[1] $C_{80}H_{120}O_5$; and 70 per cent. of the succino-resinol ester of succinic acid. From the last-named body they isolated the free *succino-resinol*, $C_{12}H_{20}O$, as a white powder melting at 275°, and possessing the usual characters of a resin alcohol.

Small quantities of sulphur are present in most varieties of amber. Gedanite is said to be free from this element, although its main constituents are identical with those of ordinary succinite. Glessite differs from succinite in the absence of the bornyl radical, which is replaced by the carvyl group. Free succinic acid is stated by P. Dahms to be present in amber in proportions ranging from 3 to 8 per cent., but its presence is denied by other observers.

Amber is soluble only to a small extent in most of the usual organic solvents. Dichlorhydrin is one of its best solvents. In alcohol, methyl alcohol, petroleum-ether and acetone amber is practically insoluble either before or after melting, and in acetic acid, ether, amyl alcohol, benzene and chloroform before melting, when it is partially soluble in carbon disulphide and oil of turpentine. Amber after melting is partially soluble in ether, amyl alcohol, acetic acid, and chloroform, and almost entirely soluble in benzene, carbon disulphide, and oil of turpentine.

The following analytical characters of genuine amber have been recorded:—

[1] On treatment with alcoholic potash, succino-abietic acid is decomposed with formation of a dibasic alcohol, *succino-abietol*, $C_{40}H_{60}O_2$, and *succino-sylvic acid*, $C_{24}H_{36}O_2$.

	R. WILLIAMS.	A. KREMEL.
Water, per cent.,	1.05	—
Ash, per cent.,	0.28	—
Acid number,	15.4	33.4 to 34.4
Ester number,	71.4	74.5 to 91.1

A sample of natural amber having a total saponification-number of 144.8, was found by von Schmidt and Erban to give the figure 36 after melting, thus showing that this process resulted in the destruction of the greater part of the esters.

IMITATION AMBER is manufactured to a certain extent from the shavings of amber produced when the pieces are trimmed. Very strong pressure is used, and although the resin is all genuine amber, the peculiar method of aggregation of its particles causes it to differ in its physical properties from natural amber, so that the term "spurious amber" appears to be justifiable. Sometimes, however, colophony and other resins are worked in. Genuine amber is doubly refracting, and when viewed by polarised light (with crossed Nicol-prisms), it shows only very faint colours, whereas the want of optical homogeneity of the pressed article causes it to exhibit brilliant interference tints.

On dry distillation, amber yields water, succinic acid and small amounts of volatile fatty acids, and a camphor-like body, together with oil of amber. *Amber pitch* remains as a black shining resin, which is easily soluble in turpentine and linseed oils, and finds valuable application in the manufacture of varnishes and lacquers.

OIL OF AMBER (*Oleum succini*), obtained by destructive distillation of amber, has a limited use in medicine. Authentic samples of amber oil examined by E. J. Parry had a specific gravity of about 0.950 and an optical rotation of about +15°. According to Schimmel & Co. (*Semi-Annual Report*, April, 1903), the pure oil differs markedly from the commercial article, the optical rotation of the former ranging from + 22.5° to + 26°, and that of the commercial oils from —2° to + 13°. There is no doubt that commercial oil of amber is almost entirely distilled from cheap resins other than amber.

Colophony. Common Rosin.

Common rosin or colophony is the fixed residue obtained by the distillation of the turpentine or oleo-resin obtained from various species of pine, but chiefly from *Pinus Australis*, *P. tæda*, *P. pinaster*, and *P. laricio*.[1]

[1] After distillation of the essential oil the melted resin is removed from the stills and run through wire-strainers into barrels. The lightest-coloured rosin is obtained from trees which have been tapped for the first time, and it then constitutes about 80 per cent. of the oleo-resin. In subsequent years the proportion of resin in the crude turpentine gradually increases, and the resin from a given tree also becomes darker year after year.

Colophony, or rosin, is a transparent or translucent resin of a faint terebinthinate odour. It is nearly tasteless, but some varieties possess a nauseous and highly characteristic after-taste.

Colophony is very brittle, and shows a shallow conchoidal fracture when broken. It varies in colour from a pale amber to dark reddish brown. The darkest kind is known commercially as "black rosin." "White rosin" is a light-coloured variety which is opaque owing to the presence of water, on the gradual evaporation of which it becomes translucent. Powdered rosin is white or pale yellow. Colophony has no sharply-defined melting point. It softens at about 70° to 80° C., becomes semi-fluid in boiling water, melts completely at a somewhat higher temperature (some varieties about 130°), and when more strongly heated in the air ignites and burns with a yellow and very smoky flame, leaving a trifling quantity of ash. On blowing out the flame a highly characteristic odour may be observed.

The specific gravity of colophony is usually between 1.07 and 1.08, the extreme figures being 1.04 to 1.10. It may be conveniently determined by immersing small pieces free from air-bubbles in brine, until they remain suspended in the liquid, and then determining the density of the saline solution.

Colophony is quite insoluble in water, though it contains small proportions of soluble bodies. At 60° C. it is slowly soluble in an equal weight of alcohol or glacial acetic acid, and is also readily dissolved by methyl and amyl alcohols, acetone, ether, chloroform, carbon disulphide, alkalies, and the fixed and volatile oils. Colophony dissolves in benzene, and more or less perfectly in petroleum-spirit.

Abietic or Sylvic Acid.

The chemistry of colophony has been the subject of various researches, with curiously conflicting results. According to Maly, the principal constituent of colophony is *abietic anhydride*, $C_{44}H_{62}O_4$; but this statement is at variance with the ready manner in which colophony reacts with alkalies. On boiling the resin with 80 per cent. alcohol, filtering hot, and adding a little water, *abietic acid* separates in a crystalline state. For the preparation of pure abietic acid from colophony, Mach treats the resin for a long time with 70 per cent. alcohol, and crystallises the undissolved portion from 90 per cent. alcohol. After 30 recrystallisations a pure white substance was obtained, which began to soften at 148°, and melted when slowly heated at 153° to 154° C. Another specimen of abietic acid was prepared from the same rosin by dissolving the crude acid in 95 per cent. alcohol, saturating the solution with hydrochloric acid gas, and recrystal-

lising the precipitate four times from methyl alcohol (*Monatsh. f. Chemie*, xiv, 186; xv, 627). According to W. Fahrion (*Zeits. angew. Chem.*, 1901, xiv, 1197, 1208, 1252), abietic acid exists (probably with isomeric acids) in colophony in an amorphous form, which on treatment with dilute alcohol, or when acted on in alcoholic solution with hydrochloric acid gas, is converted into a crystallisable modification which melts at a higher temperature, and is reconverted into the amorphous form by prolonged heating, secondary products being also formed.

Maly ascribes to abietic acid the formula $C_{44}H_{66}O_5$, while Mach, as the result of combustion-experiments, supported by cryoscopic and ebullioscopic determinations, assigns to it the composition $C_{19}H_{28}O_2$. Other observers consider abietic acid to be identical with *sylvic acid*,[1] and give it the formula $C_{20}H_{30}O_2$.[2] Some regard abietic acid as identical with Maly's *pimaric acid*[3] from gallipot and Bordeaux turpentine, but Mach denies that it is either identical or isomeric with the latter body. The melting point of abietic acid is very variously stated, Mach giving it as 153° to 154°, Dragendorff at 144°, and others again as high as 165°. Even the statements made respecting the sign of the optical rotation are discordant, a fact which suggests that two distinct varieties of abietic acid exist, as is the case with the closely analogous pimaric acid. On slow evaporation of its alcoholic solution, abietic acid is deposited in crystalline laminæ. According to Mach, it exhibits, in alcoholic solution, a specific rotation of + 66.66° for the sodium ray. Prolonged heating is stated to convert abietic acid into its anhydride.

[1] Sylvic acid is stated by S. Haller (*Ber.*, xviii, 2165) to soften at 145° and melt at 161° to 162°. When repeatedly recrystallised from alcohol, it exhibited, in alcoholic solution, a constant specific rotation of $[\alpha]_D = -53°$.

[2] W. Fahrion adopts the formula $C_{20}H_{30}O_2$ for abietic (sylvic) acid, and confirms the following constitutional formula proposed by Bischoff and Nastvogel:—

```
CH : C(CO2H) . CH . CH . CMe = CH
|                  |    |          |          (Pr = Propyl).
CH2 . CHPr    —    CH . CH . CHPr . CH2
```

Fahrion *has shown that abietic acid is very liable to spontaneous* oxidation, and this is the cause of the low values for carbon and hydrogen obtained by *certain* other workers on this substance.

[3] While agreeing in ascribing to pimaric acid the formula $C_{20}H_{30}O_2$, observers differ greatly as to its characters. According to A. Vesterberg (*Ber.*, xviii, 3331; xiv, 2167; xx, 3248), two varieties of pimaric acid exist. *Dextropimaric acid* has a specific rotation in alcoholic solution of + 72.5°, melts at 210° to 211°, and distils in a vacuum almost unchanged and without formation of sylvic acid. Ammonium dextropimarate is said to separate in fine needles when an ethereal solution of the acid is agitated with ammonia. *Lævopimaric acid* is very strongly lævorotatory ($[\alpha]_D = -272°$), and melts between 140° and 150°. S. Haller (*Ber.*, xviii, 2165) describes pimaric acid as optically inactive, and melting at 149°. Pimaric acid is said to differ from abietic acid in having a bitter taste.

Abietic acid is quite insoluble in water, but dissolves readily in strong alcohol, ether, chloroform, benzene, carbon disulphide, and glacial acetic acid. According to Mach, abietic acid dissolves in strong sulphuric acid with red colour.

According to W. Fahrion, abietic acid oxidises spontaneously with formation of *peroxides* containing $C_{20}H_{30}O_4$ and $C_{20}H_{30}O_6$. These bodies are insoluble in petroleum-spirit, but undergo intermolecular change with formation of *dioxy-abietic* and *tetroxy-abietic acids*, $C_{20}H_{29}(OH)O_3$ and $C_{20}H_{28}(OH)_2O_4$, which are soluble in petroleum spirit. The latter acid is also produced by the oxidation of abietic acid by permanganate in alkaline solution. Other indefinite products are also formed by the oxidation of abietic acid and occur in colophony.[1]

Abietic acid is frequently described as dibasic, but the presence of only one carboxyl-group in the molecule and the proportion of alkali required for its neutralisation conclusively negative this view. Abietic acid forms a series of salts, some of which are crystallisable. The abietates of the alkali-metals are readily soluble in water, alcohol, and ether, and are possessed of marked detergent properties. Hence the employment of rosin in soap-making. An acid potassium abietate, obtained by Mach by neutralising an alcoholic solution of abietic acid with alcoholic potash, or boiling it with potassium carbonate, forms bundles of silky needles melting at 183°. The neutral potassium salt also crystallises in silky needles, while the barium salt is described as a white, amorphous compound, becoming yellow on exposure to air.

According to Perrenoud, the ammonium salt of abietic acid from colophony is gelatinous, whereas the acid ammonium salt of pimaric acid crystallises in handsome needles.

The *acid number* of colophony normally ranges between 155 and 175. This represents a proportion of resin acids, in terms of $C_{20}H_{30}O_2$, ranging from 83.4 to 93.8 per cent. In addition to the free acid number obtained by direct titration of the resin in alcoholic solution with caustic alkali and phenolphthaleïn, colophony neutralises a small additional quantity of alkali on complete saponification. This additional neutralising power may be due to the presence of resin-esters, the existence of which is, however, denied by several authorities; to the hydro-

[1] F. Jean (*Chem. News*, 1872, xxvi, 207) has described three acid resins as occurring in colophony. Resin A, probably identical with abietic acid, is insoluble in water, but soluble in alcohol, ether, and oil of turpentine. Resin B is insoluble in the last solvent, and is also distinguished from A by yielding a sodium salt insoluble in caustic soda solution of 1.116 sp. gravity. Resin C is soluble in water, and its aqueous solution is precipitated by silver and cupric salts. Tschirch and Studer claim to have isolated three isomeric abietic acids from American colophony. Two of the acids form insoluble lead salts (*Arch. der Pharm.*, 1903, ccxli, 495).

lysis of abietic anhydride; or to the hydrolysis of lactone acids. Any of these explanations is compatible with the facts observed, which at present do not support any view to the exclusion of the others.

Colophony also contains a small percentage of matters which resist saponification. These probably consist chiefly of hydrocarbons of the nature of rosin oil, produced by the action of heat on the colophony during the process of manufacture.

The following table shows the acid and saponification numbers recorded for various samples of commercial rosin. The ester-numbers are the differences between the two former figures.

KIND OF ROSIN.	ACID NUMBER.	ESTER NUMBER.	SAPONIFICATION NO.	OBSERVER.	REFERENCE.
American (6 samples),	154.1 to 164.6	15.7 to 30.0	174.7 to 194.3	J. Lewkowitsch	*J. S. C. I.* xii, 505.
Austrian,	146.0	21.1	167.1	v. Schmidt & Erban	*J. S. C. I.* viii, 308.
Typical (6 samples)	154.0 to 162.0	14.4 to 19.8	174.3 to 177.6	Smetham & Dodd	*J. S. C. I.* xix, 102.
White,	172	7.0	179	H. Amsel	*Zeits. ang. Chem.*, 1896, p. 429.
Yellow; new,	162	7.0	169	"	*Ibid.*
Yellow; old,	167	8.0	175	"	*Ibid.*
Very pale,	155	12	167	A. H. Allen	Unpublished note.

In addition to the above data, A. Kremel (*Pharm. Jour.* [3], xvii, 547) found acid-values varying from 151.1 in dark Austrian colophony to 173.6 in an American specimen. Beckurts and Brüche have recorded 180, 181, and 185 as the acid-values of samples of white, brown, and yellow rosin respectively, and give identical figures for the saponification values of the same samples, a result which is improbable. In red rosin they found acid-values ranging from 173 to 186, with saponification-numbers from 179 to 193. R. Williams has published the results yielded by four samples of rosin (*Chem. News*, lviii, 224), but the figures are admittedly abnormal.

Two samples of American colophony analysed in the author's laboratory (1903) by S. O. Richmond gave the following results:—

	PALE.	BROWN.
Specific gravity,	1.069	1.081
Acid-number (by titration with aqueous alkali, A),	157.9	172.4
Acid-number (by titration with alcoholic alkali, *a*),	154.0	168.4
Total saponification-number (B),	169.4	176.2
Ester-number (B—A),	11.5	3.8
Ester-number (B—*a*),	15.4	7.8
Unsaponifiable matter, per cent.,	9.25 9.93	4.28

It will be observed that the figures obtained by dissolving the sample in strong alcohol, and titrating the solution with alcoholic caustic alkali, are somewhat lower than those obtained when seminormal aqueous caustic soda was employed for the titration, but the differences are not great. As the total saponification-number was determined by titrating back the alcoholic alkaline liquid with aqueous hydrochloric acid, the figures for free acid obtained by titration with aqueous alkali have been used in calculating the following composition of the samples from the data recorded above:—

	Pale.	Brown.
Abietic Acid ($C_{20}H_{30}O_2$),	85.16 per cent.	92.96 per cent.
Abietic Anhydride ($C_{40}H_{58}O_3$),	6.04 "	1.99 "
Hydrocarbons (unsaponifiable matter),	9.25 "	4.28 "
	100.45	99.23.

These results show that the samples examined consisted chiefly of abietic acid, and did not contain any large proportion of abietic anhydride or lactone-acids. The unsaponifiable matter was of a very pale straw-yellow colour. That from the pale rosin was soft and "tacky," but that from the brown sample was somewhat harder.

The sample of pale rosin described above was also examined by Tschirch's process (page 142) with the following results:—

		Per Cent.	Combining Weight.
Resin Acids,	soluble in 1% Ammonium Carbonate solution,	2.62	326.6
	soluble in 1% Sodium Carbonate solution,	88.62	343.9
	soluble in 1% Sodium Hydroxide solution,	0.64	
Unsaponifiable Matter,	volatile with steam (terpenes),	1.00	7.05[1]
	not volatile with steam,	6.05	
		98.93	

The original sample of pale rosin, and the separated resin acids and unsaponifiable matter, all gave a fine purple coloration, fading slowly to brown, when they were dissolved in a little acetic anhydride, and a drop of sulphuric acid (sp. gr. 1.53) added. When dissolved in acetic anhydride and a drop of stannic tetrabromide added, a purple coloration was produced in each case, the colour fading slowly to dark brown.

Holde and Marcusson (*Analyst*, 1902, xxvii, 252) state the average amount of *unsaponifiable matter* in colophony at 8 per cent. The highest recorded amount is 15.94 per cent., which

[1] It will be observed that the proportion of unsaponifiable matter isolated is materially less than that previously found.

was found by J. Lewkowitsch in a sample having an acid-value of 146.5 and a saponification-value of 153.0.

Two samples of colophony recently examined by Rowland Williams (private communication to author) gave the following results[1] :—

	A.	B.
Acid-number, by titration with alcoholic alkali (a),	166.3	166.8
Total saponification number (B),	171.4	170.7
Ester-number (B — a),	5.1	3.9
Unsaponifiable matter,	5.66 per cent.	6.25 per cent.

K. Dieterich has determined the *acetyl-value* of colophony, and obtained the following results:—

By titration of the acetylised resin with alkali,	*155.8*
By back-titration, after saponification (ester number),	92.1 to 95.4
Difference (= saponification-number of acetylised resin),	251.2 to 274.

Kitt has found the *carbonyl-value* of colophony to be insignificant (about 0.5 per cent.).

Gregor and Bamberger obtained negative results for the *methoxyl-value* of colophony.

The *iodine-number* of colophony has been determined by various observers with curiously variable results (pages 150, 193).[2] The determination has a practical value for the detection of

[1] The following figures show the composition of the samples calculated from the data of R. Williams and Lewkowitsch:

	Williams. A.	Williams. B	Lewkowitsch.
Abietic acid,	89.52 per cent.	89.53 per cent.	78.86 per cent.
Abietic anhydride,	3.66 "	2.04 "	3.39 "
Hydrocarbons (unsap. matter),	5.66 "	6.25 "	15.94 "
	98.84	97.82	98.19

[2] The figures are generally stated to range from 120 to 185. Smetham found the iodine absorption of colophony to range from 159 to 185, when treated with Hübl's solution for eighteen hours. Smetham finds great care to be necessary to obtain comparative results, it being very important that the time of treatment and other conditions of the determination should always be identical. Higher figures were obtained by Wijs' than by Hübl's original method. P. C. McIlhiney (*J. S. C. I.*, 1894, page 668) found the iodine absorption of a sample of colophony by Hübl's method to range from 127 to 173, according to the length of time allowed for the reaction.

The *bromine-absorption* of colophony, according to McIlhiney, is a more reliable constant than the iodine absorption. The bromine-absorption was found to vary in the same sample from 161 per cent. after two minutes' action (the bromine being in solution in carbon tetrachloride) to 178 after seventy minutes, and to 213 after twenty hours. An excess of 100 per cent. of bromine is required for the speedy completion of the reaction. The presence of water does not affect the results, and a raised temperature has very little disturbing effect.

colophony in shellac, but the recorded figures should be verified by examining a typical sample of colophony side-by-side with the shellac in question.

Colophony is used very largely in the manufacture of soap, for the preparation of varnish and resinates used as driers, and to a certain extent in pharmacy, especially in veterinary practice. It is also employed as an adulterant of the more expensive resins, such as shellac, dammar, and dragon's blood. It is largely distilled for the manufacture of rosin oil.

According to W. Fahrion, colophony for use in varnish manufacture should be light in colour and have a high acid number, while the ester number, unsaponifiable matters, and substances insoluble in petroleum-spirit should be as low as possible.

Detection and Determination of Colophony.

When unmixed with interfering substances colophony is readily recognised by its physical and sensible characters (page 158).

A valuable reaction for colophony, originally suggested by Liebermann, but modified by Storch and Morawski, consists in treating the substance with acetic anhydride, cooling the liquid, and separating the acetic anhydride with a pipette or other suitable arrangement. Sulphuric acid of 1.53 specific gravity is then allowed to flow gently into the tube containing the acetic anhydride, when a reddish-violet colour will be immediately produced at the junction of the two liquids if colophony be present. The colour soon changes to reddish-brown. In the author's experience, a preferable plan is to place from ten to twenty drops of the acetic·anhydride solution in a flat porcelain dish (or the inverted cover of a porcelain crucible), and cautiously add a drop or two of sulphuric acid of the above strength. The coloration is seen more readily against a white background than when a test-tube is used.

Fatty acids do not produce a similar colour, but cholesterin and some other bodies simulate the reaction of colophony. Cholesterin may be separated by shaking the substance with aqueous soda and ether, separating the alkaline liquid, and acidulating it with sulphuric acid. The precipitate of resin acids should be separated and dissolved in acetic anhydride.

Other qualitative tests for resin acids and approximate methods of separating them from fixed oils, &c., are described in Vol. II, Part I.

A fair approximate determination of rosin when in admixture with neutral fatty oils may be effected by dissolving the sample in a mixture of alcohol and ether, and titrating with standard caustic soda solution. Taking 165 as the average acid-number of colophony, each cubic centimetre of decinormal alkali neutral-

ised by the sample represents 0.0340 gramme of colophony present. As the neutralising power of rosin varies materially, the result obtained as above can only claim approximate accuracy. It is, of course, further affected by free fatty acids, which, if present in quantity, will entirely vitiate the determination. The process is, however, convenient and of considerable practical utility. Thus, the author has employed it for approximately determining the proportion of rosin in a mixture of that substance with linseed oil used as *bird-lime*.

For the determination of colophony in cerasin and paraffin, the sample should be boiled several times with 70 per cent. alcohol. The alcoholic liquid is filtered wheu quite cold, and the filtrate distilled. The residue of resin is dried at 110° to 115° C. and weighed. If fatty acids are present, they will be extracted with the resin and must be subsequently separated.

The separation of fatty and resin acids is necessary for the determination of colophony in soap. It presents considerable difficulties, as the fatty acids vary somewhat in chemical and physical characters according to their source, and colophony is itself of complex and variable composition. The processes practically available are those of Barfoed, Gladding and Twitchell, or modifications or combinations of these. These methods are fully described in Vol. II, Part I. Twitchell's is by far the most satisfactory process, and is sufficiently accurate for many purposes. When, however, it is desired to estimate the proportion of colophony in soap with the greatest attainable accuracy, a combination of Twitchell's and Gladding's methods described by Holde and Marcusson (*Analyst*, 1902, p. 252) may be advantageously employed. In this process special attention is paid to the washing of the immiscible solvents employed, the resin acids soluble in water are recovered, and the unsaponifiable matter natural to the colophony is determined or allowed for. The process is as follows:—

A quantity of the sample representing about 5 grammes of fatty and resin acids is boiled with 50 cc. of alcoholic potash for half an hour under a reflux-condenser. The alcoholic solution is then evaporated, the residue dissolved in water, and any unsaponifiable matter removed by agitation with ether. The aqueous layer is separated and acidified with hydrochloric acid. Soaps containing no unsaponified fat or unsaponifiable matter may be directly dissolved in water and decomposed with acid. The separated acids are removed by shaking with ether; the aqueous acid solution is neutralised, evaporated to about 25 cc., re-acidified, and shaken out with ether. After distilling off the ether from the united ethereal extracts, the residue of resin and fatty acids is dissolved in 50 cc. of absolute alcohol, and the fatty acids converted into esters by passing a moderately

rapid current of dry hydrochloric acid gas through the solution cooled by ice-water to a temperature not above 10° C. When the operation is complete (which is usually the case in from one to two hours), the liquid is allowed to stand for half an hour at the ordinary temperature. It is then diluted with five times its volume of water, and boiled under a reflux-condenser for half an hour. The cooled solution is agitated with several successive quantities of ether until the extracts are colourless. The aqueous liquid is neutralised, evaporated to 50 cc., acidified, and repeatedly extracted with small quantities of ether to recover the water-soluble constituents of colophony. The mixed ethereal solutions are shaken out with about 50 cc. of a solution containing 10 grammes of caustic potash, 10 grammes of alcohol, and 100 cc. of water, when a brown layer usually separates out between the ether and the alkaline solution, and is drawn off with the latter. This layer contains a considerable portion of the resin-soap, which is only slightly soluble in the potash solution. The ether is shaken with water to remove soluble resin-soaps; then with two successive quantities (10 cc.) of the potash solution; and finally with water until the washings are colourless.[1] The alkaline liquid is now acidified and agitated with ether until completely extracted. The acid solution is neutralised, evaporated to a small bulk, re-acidified, and again shaken out with ether. The total ether extracts are washed with 20 cc. of water, and the ether distilled off. The residue of resin-acids so obtained—still contaminated with unchanged fatty acids—is treated with several small successive additions of absolute alcohol to remove the last traces of water, and weighed. The fatty acids still remaining in the resin-acids are removed by Gladding's process. From 0.4 to 0.6 gramme of the resin-acids, obtained as above, should be placed in a 100 cc. stoppered and graduated cylinder, and dissolved in 20 cc. of 95 per cent. alcohol.[2] A drop of phenolphthaleïn solution is added to the alcoholic solution, and then concentrated caustic soda solution (1 of NaOH to 2 of water) until the reaction is just alkaline. The loosely-stoppered cylinder and its contents are heated for a short time in the water-bath, then cooled, and ether added up to the 100 cc. mark. One gramme of dry powdered silver nitrate is added, and the contents of the cylinder are shaken for 15 minutes to convert the fatty and resin acids into silver salts.

[1] In the presence of fish-oil acids or much colophony the washing with water must be very thorough.

[2] If only a small amount of resin-acid is obtained, the prescribed proportions of the ether-alcohol mixture must be correspondingly altered, whilst in the case of a large yield of acids, it is advisable to dissolve the whole in so much 95 per cent. alcohol that 20 c.c. of the solution shall contain 0.5 gramme of resin-acids.

When the insoluble salts have completely settled (preferably after standing overnight), 70 c.c. of the solution should be pipetted into a second 100 c.c. cylinder and shaken with 20 c.c. of dilute hydrochloric acid (1 : 2). The ethereal layer is drawn off, and the aqueous liquid twice shaken with ether. The united ether-extracts are washed with water, filtered, and the ether distilled off. The residue, amounting to about 10 cc., is evaporated, dried for a short time at 110° to 115° C., and weighed. The weight of the resin-acids so found is calculated back into the first weight (impure acids) obtained, and then on the original substance taken. The percentage found is corrected by the subtraction of 0.4 per cent., this allowance being made for a small amount of unesterified fatty acid which is always present. As colophony contains an average of 8 per cent. of unsaponifiable matter, a second correction is necessary, the true percentage of colophony of the substance under examiuation being found by the following equation, in which the corrections are combiued:—

$$100 \frac{(\text{Percentage of resin acids found} - 0.4)}{92} = \text{percentage of colophony.}$$

COLOPHONATES. RESINATES.

Colophony dissolves in solutions of caustic alkalies and of alkali-metal carbonates, with formation of so-called *resin soaps*, consisting of impure abietates.

Sodium "resinate" may be prepared by dissolving 30 parts of caustic soda in 900 parts of water, and gradually adding 180 parts of rosin. Upon cooling, the resin soap separates as a yellow pasty mass, which is drained from the liquid and heated to 100° C. till it becomes dry and friable, when it may be reduced to powder. The product thus obtained is brown and somewhat resembles powdered rosin, but is deliquescent and very soluble in water. The taste is resinous and very acrid. Resiu soaps differ from those of the fatty acids in not being readily precipitated from their aqueous solutions by addition of brine. Resin soaps are also differentiated by their solubility in ether or ether-alcohol, a fact utilised by Barfoed for the separation of fatty from resin acids. Jean and Remont have proposed to utilise the solubility of barium colophonate in alcohol to effect the same separation, while Gladding has described a method of separating fatty from resin acids based on the ready solubility of silver colophonate in ether, and the almost complete insolubility of silver oleate, &c., in the same menstruum, even in presence of some alcohol.

Potassium and sodium resinates have marked detergent properties, and are extensively employed in the manufacture of the commoner kinds of soap.

Resin soaps have a remarkable emulsifying power (see H. Collier, *Pharm. J.* [3], xx, 751), and this property finds an extensive application in the manufacture of sheep-dips and phenolic disinfecting fluids. Creolin, lysol, Little's sheep-dip, and Jeyes' fluid are examples of such preparations. (See Vol. II, Part II.)

Certain metallic resinates, especially those of manganese and lead, are often added to boiled linseed oil, and are extensively employed in the manufacture of varnishes. They are made either by melting the resin with the oxide of the metal the resinate of which is required, or by the addition of a soluble metallic salt to the aqueous solution of a resin soap. Commercial resinates so made are of very variable composition, and often contain a considerable proportion of uncombined resin. The following data respecting the composition of commercial resinates are due to H. Amsel (*Zeits. angew. Chem.*, 1896, p. 429; *Analyst*, xxi, 261):—

	Mineral Matter.		Acid Value.	Sapn. No.
1. Resinated Manganese Extract, ...	8.9	per cent.	116	195
2. Manganese Resinate (melted), ...	4.19	"	75	171
3. " " (precipitated), ..	10.91	"	118	185
4. Lead and Manganese Resinate (I), ...	10.4	"	75	151
5. " " " (II), ..	12.09	"	46	134
6. Lead Resinate (melted), ...	20.76	"	47	130
7. " " (precipitated), ...	25.3	"	37	128
8. " " (I), ...	28.47	"	45	126
9. " " (II), ...	11.7	"	103	165
10. " " (III), ...	29.39	"	40	128

The mineral matter, which is regarded by Amsel as representing fairly accurately the metallic oxide, was determined by incineration of the sample in a porcelain crucible. For the determination of the acid value about 2 grammes weight of the sample was dissolved in 25 c.c. of a mixture of equal volumes of alcohol and ether, and titrated with seminormal alcoholic potash and phenolphthaleïn. The saponification-numbers were determined in the usual way, but the figures are vitiated by the interfering action of the metallic oxides.

Amsel extracts free resin acids from commercial resinates by treatment with a 1 per cent. solution of ammonia, but admits that the method is not free from objection. He suggests that petroleum-spirit might be employed.

M. Weger (*Zeits. angew. Chem.*, 1896, 531; *Analyst*, xxi, 300) thinks the proportion of free resin found by Amsel to be exaggerated and points out that the total ash affords very insufficient information respecting the potential amount of metallic oxides present, since only such proportions as are soluble in cold ether or chloroform have any efficiency. The amount of manganese resinate soluble in ether, or of lead resinate in chloroform,

is practically the same as the amounts dissolved by hot linseed oil. Precipitated manganese resinate does not occur in commerce, and the fused substance commonly contains from 9 to 9½ per cent. of soluble manganese, though as much as 11 per cent. has been met with. Only lead and manganese resinates are used for driers. Barium, calcium, and zinc resinates are sometimes mixed with copal, but if no manganese or lead be present the preparations are valueless for varnish-making. The larger the proportion of soluble lead or manganese in a resinate, in the absence of insoluble matter, the less is required to be added to a linseed oil.[1] From 1 to 3 per cent. of the resinate is required for the preparation of a good varnish.

Dry Distillation of Colophony.

When rosin is subjected to dry distillation, it undergoes decomposition in a very complex manner.[2] Besides a variable proportion of unaltered resin, it yields a large number of hydrocarbons, traces of phenoloid bodies, and various acids and aldehydes of the fatty series. Among the last named have been recognised acetic, propionic,[3] isobutyric, isovaleric, caproic,

[1] The linseed oil is heated to about 120° (not above 150°), or preferably one part of the resinate is dissolved in two parts of linseed oil at 120°, and the mixture stirred into the main bulk. The oil can be oxidised either before or after the addition of the drier. For clear varnish lead-manganese resinate is used, and where all separation is to be avoided, melted manganese resinate.

Notwithstanding the fact that the proportion of resinates used as driers rarely exceeds 3 per cent., the author has experience of a number of cases in which unsaponifiable matter having all the characters of rosin oil has been isolated from boiled linseed to the extent of 5 per cent., and its presence has been "explained" on the ground that it was a natural and unavoidable constituent of the resinate employed as a drier! Five per cent. of unsaponifiable matter would represent from 80 to 100 per cent. of resinates in the oil, against 3 per cent. ordinarily added.

[2] According to Bischoff and Nastvogel (*Ber.*, xxiii, 1919; *J. S. C. I.*, ix, 927), if rosin be distilled in a vacuum the products are fewer and more readily separated than when the distillation is conducted at the ordinary atmospheric pressure. Working on laboratory quantities, by repeated fractionation under 30 mm. pressure, two main fractions were obtained. The larger of these boiled at that pressure between 248° and 250°, and after a short time solidified to a colourless, brittle, microcrystalline mass, which was insoluble in water, but soluble in alcohol and ether. It had the composition $C_{40}H_{58}O_3$, and was apparently *abietic anhydride* ("isosylvic anhydride"). It had a specific rotation of + 63°, dissolved in a warm solution of caustic potash, and on acidulating the liquid with acetic acid gave an acid having the composition $C_{20}H_{30}O_2$, and melting at 60.5° to 62.5°. Hence it was an isomer of abietic or sylvic acid. The other main fraction boiling at 318° to 320° contained $C_{20}H_{32}$, and was a diterpene probably identical with Deville's *colophene*.

[3] Propionic acid was observed by Renard in considerable quantity in the products of the distillation of rosin at a red heat.

heptoic, nonoic, and heudecatoic acids; and isobutyric and valeric aldehydes.

The distillation of rosin is practised commercially on an extensive scale for the production of resin spirit and resin oil. The process is conducted in vertical cast-iron stills with hemispherical ends. The heat is applied directly, and distillation without steam is usually preferred, as in that case the production of spirit is less. Gas and aqueous liquid are first given off, followed or accompanied by a light, oily liquid, which boils between 80° and 250°, and constitutes the product known as *resin spirit* (see below). At about 300°, or somewhat above, *rosin oil* commences to distil, and continues to pass over until the still attains a dull red heat. Water, containing a little acetic acid, continues to pass over throughout the process, and gases are evolved in considerable quantity.[1] The residue in the still consists of pitch or coke, according to the stage to which the distillation is pushed. The yield of rosin oil is generally about 85 per cent., the remaining 15 per cent. including from 2½ to 5 per cent. of rosin spirit, a small proportion of water, containing about 1 per cent. of acetic acid (*J. S. C. I.*, ix, 16), pitch or coke, gases, &c.[2]

RESIN SPIRIT.

Resin spirit is the lighter and more volatile oily portion of the product of the dry distillation of rosin. It is separated from the acetous aqueous liquid which distils with it, purified by agitation with sulphuric acid and caustic soda (and sometimes common salt), and is then redistilled.

When thus refined, resin spirit is a colourless liquid, insoluble in water or alcohol, but miscible in all proportions with ether, petroleum spirit, and oil of turpentine. Resin spirit presents a close general resemblance to oil of turpentine, for which it is extensively used as a substitute and adulterant. The odour of resin spirit, however, is peculiar, and the specific gravity is more variable, ranging from 0.856 to 0.883. The behaviour of resin spirit on fractional distillation is also different from that of turpentine oil, and other distinctions exist (see Turpentine Oil).

Resin spirit has a peculiar and highly complex composition. According to A. Renard (*Ann. Chim. Phys.* [6], i, 223; abst.

[1] The gases contain carbon monoxide, ethylene, butylene, and pentine, and are said to be powerfully anæsthetic.

[2] E. J. Mills has recorded the densities and bromine-absorptions of the products distilling at frequent intervals during an entire operation. The density increased from 0.909 to 1.0030 at the end of twenty hours, and then fell to 0.970. The bromine-absorption of the first product was 142 per cent. and gradually fell to 32 per cent. (*J. S. C. I.*, iv, 328).

Jour. Chem. Soc., 1884, xlvi, 843), the hydrocarbons of resin spirit include pentane, pentene, and their homologues; toluene and its homologues; tetra- and hexa-toluene, and their homologues; terpenes; &c.[1] Deville found colophene (boiling between 318° and 328°) in the last fractions of resin spirit.

About one-half of resin spirit consists of hydrocarbons boiling below 120° C.

One of the most characteristic constituents of the lighter fractions of resin spirit is the hydrocarbon *heptine*, C_7H_{12}, which appears to have the constitution of a *methyl-propyl-allene*. It boils at 103° to 104°, and has a specific gravity of 0.8031 at 20° C. Heptine is colourless, mobile, of characteristic odour, and is soluble in alcohol and ether. It absorbs oxygen very readily, and is without action on an ammoniacal solution of cuprous chloride or silver nitrate. By treatment with concentrated sulphuric acid it is polymerised, with formation of a *di-heptine* $C_{14}H_{24}$, boiling at 235–250°, and rapidly oxidising and resinifying in the air. By the action of water and air it is converted into a crystalline *heptine glycol*, $C_7H_{12}(OH)_2,H_2O$, soluble in water, alcohol, and ether. The crystals, as also the original hydrocarbon, when warmed with an acid (*e. g.*, hydrochloric, sulphuric, tartaric), give a series of colorations, the mixture passing through shades of yellow, red, green, and deep blue; and on adding this liquid to alcohol a magnificent green colour is communicated to it (G. H. Morris, *Jour. Chem. Soc.*, 1882, xli, 172). Resin spirit itself does not give the reaction distinctly, and the author has not succeeded in applying it to the detection of resin spirit in turpentine oil.

Rosin Oil.

Rosin oil, or *Resin oil*, is the heavier and less volatile portion of the product resulting from the dry distillation of colophony. The crude oil first obtained can be purified by washing with a small percentage of sulphuric acid, followed by treatment with lime-water and redistillation, with or without the aid of steam. A superior product is obtainable by redistilling the oil over solid caustic soda, with the aid of a current of superheated steam. Lime-dust and other reducing agents have also been employed, and a very fine oil is said to be obtainable by mixing the crude oil with cottonseed oil prior to distillation.

Commercial rosin oil is a viscid liquid varying in colour from water-white to dark brown, and is sometimes opalescent from the presence of water. It generally exhibits a strong bluish

[1] For a complete list of the constituents of resin spirit, with their formulæ and boiling points, see E. M. Holmes, *Pharm. Jour.*, 1899, i, 99. G. H. Morris has published a valuable list of researches on resin spirit prior to 1882 (*Jour. Chem. Soc.*, xli, 172).

or violet fluorescence, which is apparent even in its dilute ethereal solutions. The bloom is less marked in refined rosin oil, and can be destroyed more or less completely by exposure to air and sunlight, by treatment with hydrogen peroxide, by addition of nitrobenzene, nitro- or dinitro-toluene, dinitro-naphthalene, &c., or by heating with sulphur.

Crude rosin oil has a specific gravity ranging from 0.96 to 1.10, but when refined the figures are much more constant, being usually between 0.97 and 0.99.

Refined rosin oil has but little odour at ordinary temperatures, but when strongly heated it gives fumes having a marked odour of resin, neutral or nearly so in reaction to wet litmus-paper, and which burn, when inflamed, with a large and very smoky flame. When rosin oil is distilled, little or no distillate is usually obtained below 300° C.[1]

The taste of rosin oil is peculiar, and the after-taste strong, nauseous, and highly characteristic.

Rosin oil is insoluble in water, and but slightly soluble in alcohol, but it is miscible in all proportions with fatty oils, mineral oils, ether, chloroform, carbon disulphide, turpentine oil, and petroleum-spirit.

When treated with strong sulphuric acid, as in Maumené's test for fixed oils, rosin oil usually gives a rise of 18° to 20° in temperature, and forms a reddish-brown liquid which separates into two strata on standing.

Nitric acid is sometimes without immediate action on rosin oil, but if the mixture be warmed a violent reaction often suddenly ensues, and, after cooling, the oil is found to be converted into a more or less brittle red resin.

A. Renard has observed that anhydrous stannic chloride develops a violet coloration with rosin oil. The author has found it more convenient to employ stannic bromide than stannic chloride, and finds that the reaction is much more delicate and under control if free bromine be also present and the oil and reagent be previously dissolved in carbon disulphide. The stannic bromide is prepared by allowing bromine to fall drop by drop on granulated tin contained in a dry flask immersed in cold water. The addition is continued until the permanent coloration of the product shows that the bromine is in excess. A further moderate addition of bromine is then made, and the liquid is then diluted with three or four times its measure of carbon disulphide, in which the stannic bromide is readily

[1] However often rosin oil be distilled, the product always contains a small quantity of terpenoid bodies, which are probably produced by depolymerisation of the heavier hydrocarbons by a process of "cracking," similar to that undergone by the hydrocarbons of petroleum under the same conditions.

soluble. To employ the reagent, which when thus prepared appears to be perfectly stable, a few drops of the sample should be placed in a dry test-tube and dissolved in about 1 cc. of carbon disulphide. The bromide reagent is then gradually added, when if rosin oil be present the liquid will rapidly acquire a fine violet coloration, which in the case of pure rosin is so intense as to necessitate dilution with carbon disulphide before the colour is perceptible. On standing for some time, a deposit of violet colour is formed at the bottom of the tube, and if the remaining liquid be poured off and the residue be warmed with a little carbon disulphide, a violet or purple solution of great purity of tint may be obtained. This mode of operating is especially useful in the presence of foreign oils or impurities which disguise the colour due to rosin oil. In the presence of much mineral oil the author has found it a good plan to first mix the sample with a solution of stannic bromide in carbon disulphide, and then add, drop by drop, a solution of bromine in carbon disulphide, by which means the violet coloration may often be obtained unobscured by any colour produced by the mineral oil.[1]

The violet substance to which the coloration is due appears to be permanent in the air, but the colour is destroyed by addition of alcohol, ether, ammonia, or water.

Chloroform may be substituted for carbon disulphide in the foregoing test.

Instead of dissolving the oil in carbon disulphide it may be dissolved in glacial acetic acid, and the greater solubility of rosin oil than mineral oils in this menstruum affords a means of applying the test to mixtures of the two in a very advantageous manner. Thus, if the sample to be tested be shaken in the cold with twice its measure of glacial acetic acid, and the acid layer separated and tested with a solution of stannic bromide and bromine in carbon disulphide or chloroform, a fine violet coloration will be produced if rosin oil be present. The coloration produced in acetic acid solution appears to be of decidedly bluer shade than that obtained when carbon disulphide is used as the solvent for the oil, but the tint in the latter case varies considerably with the proportion of the reagent used, a large excess having a tendency to produce reddish tints.

When agitated with one-third of their measure of fuming hydrochloric acid, most samples of rosin oil gradually acquire a dark and ultimately a black colour.

Chlorine and bromine act somewhat violently on rosin oil. The proportion of bromine absorbed is very variable.

[1] A sample of lubricating oil from Russian petroleum (oleo-naphtha) gave a fiery red colour with the bromide reagent, a heavy oil from American petroleum gave a bright yellow, and a shale lubricating oil gave an olive-green tint.

Rosin oil is often strongly dextro-rotatory, but the optical activity is variable, being sometimes slight and occasionally left-handed. The rotation is not due simply to the presence of resin acids, as has been contended, for the hydrocarbons isolated in the author's laboratory from refined oil have exhibited a dextro-rotatory power as high as +46° for the sodium ray. To render highly-coloured rosin oil fit for optical examination, Valenta treats it with potassium ferrocyanide and then filters.

The chemical composition of rosin oil is not perfectly understood. It often contains a notable proportion of *abietic acid*, or possibly abietic anhydride, but the greater part consists of a mixture of hydrocarbons of high-boiling point.[1]

The following results of analyses of samples of rosin oil examined in the author's laboratory in 1886 show the variation in the character of the commercial article. The specific gravity was determined by the bottle, the oils being too viscous to allow a plummet being satisfactorily used. The hydrocarbons were isolated as described on page 165, and the resin acids subsequently recovered by acidulating the alkaline liquid.

Description of Sample.	Specific Gravity.	Resin Acids.	Hydrocarbons.	Bromine-absorption; Dry.		Bromine-absorption; Wet.	
				Total.	As HBr.	Total.	As HBr.
Very pale refined oil,	0.990	...	96.9	110.0	11.8	...	...
Pale oil; special,	0.982	6.4	93.9	105.1	4.8	...	...
Pale sweet oil,	0.979	1.1	...	63.0	4.7	56.5	13.6
Ordinary oil,	0.985	17.8	81.2	138.5	9.7	...	...
Common dark oil (not the commonest),	1.099	11.1	88.6	66.6	7.6	...	...
Crude oil,	0.990	...	...	60.8	3.9	47.0	11.2
Pine oil,	0.986	...	...	73.9	5.1	51.9	8.9
Ink oil,	1.006	...	...	...	...	...	...

[1] According to A. Renard (*Compt. rend.*, cv, 865; cvi, 856, 1086), about 80 per cent. of the hydrocarbon-constituents of rosin oil consists of *diterebentyl*, $H_{15}C_{10}-C_{10}H_{15}$. This body forms a colourless oil which has a gravity of 0.9688 at 18°, and boils at 343° to 346°. Its specific rotation is +59°. If a thin layer of diterebentyl is exposed to the air for some time, it absorbs about 10 per cent. of oxygen and forms a sticky varnish. When treated in the cold with strong sulphuric acid, diterebentyl yields a monosulphonic acid as a brownish-black mass soluble in water, alcohol, and ether. Its solution is fluorescent, appearing brown by transmitted and green by reflected light.

If the fraction of rosin oil boiling betwen 300° and 360° be treated with sulphuric acid, the diterebentyl becomes polymerised or converted into the sulphonic acid mentioned above. If the oily portion be separated and distilled, the distillate contains *diterebentylene*, $C_{20}H_{28}$, and *didecene*, $C_{20}H_{36}$, which together form about 20 per cent. of the hydrocarbons of rosin oil (A. Renard, *Compt. rend.*, cvi, 1086).

It will be observed that the bromine-absorptions, as determined by the dry process (Part ii, page 25) are extremely variable. There is also a wide divergence between the results by the dry and those by the wet process, and the absorptions of different samples are not even comparative. The figures obtained by the wet process are less than those yielded by the dry, while the reverse is the case with shale and petroleum products. The results were confirmed by repetition, and hence the anomalous figures are not errors of experiment.

A recent analysis (1903) of a commercial sample of rosin oil made by J. Thompson, in the author's laboratory, gave the following results:—

	Per Cent.		Combining Weight.
Resin Acids, weighed,	15.72		289
Resin Acids, titrated (as $C_{20}H_{30}O_2$),	16.91	98.62	302
Unsaponifiable Matter,	81.71		

Rosin oil has a large legitimate employment as a lubricant, especially for machinery and wagon-wheels. It is used in the condition of rosin-grease, and in admixture with olive, rape, and other oils.[1] Mixed with rape oil it has been employed for adulterating olive oil, and it is frequently added to the inferior kinds of boiled linseed oil. Castor oil has been systematically adulterated with rosin oil. Rosin oil is sometimes added to the denser kinds of mineral lubricating oil.

The detection of rosin oil in fatty oils is based on its isolation by the method described in Part i, pages 48 and 112, and its subsequent identification by its taste, odour on heating, specific gravity, optical activity, reaction with stannic bromide, and formation of a grease with slaked lime. Some of these reactions are applicable to the original mixture of fatty and rosin oils. If the accurate determination of the rosin oil be desired, it will often be necessary to add to the weight of the hydrocarbons or ether-residue that of the resin acids, after separation from the fatty acids as described in Part i, page 107.

The detection of rosin oil in admixture with the mineral lubricating oils may be effected with tolerable ease and certainty, but the positive recognition of a moderate proportion of mineral oil in such a mixture is more difficult. Any optical activity of the sample or purple reaction with stannic bromide affords definite proof of the presence of rosin oil, and in many cases its existence is evident from the taste of the sample and its odour

[1] Information respecting the mode of manufacture of rosin oil, and the composition of various lubricants containing it, will be found in the *Jour. Chem. Soc.*, vol. xxvi, pp. 304, 305, and 1175, and also in *J. S. C. I.*, 1902, p. 1336. The practical uses of rosin and rosin oil are also described in the *J. S. C. I.*, 1904, p. 328.

on heating. A high density and bromine-absorption, and a violent reaction with nitric acid, also afford strong evidence of the presence of rosin oil.

Valenta and Feigerle (*Dingl. Polyt. Jour.*, ccliii, 418; *Jour. Chem. Soc.*, xlviii, 93) employ glacial acetic acid for detecting rosin oil in mineral lubricating oils. They recommend that 2 cc. of the oil should be treated with 10 cc. of glacial acetic acid (sp. gr. 1.0562 at 15° C.), and heated for five minutes to 50° C. in a loosely corked test-tube immersed in a water-bath. The mixture is then passed through a small filter and the middle portion of the filtrate collected. A weighed quantity of the filtrate is then titrated with standard alkali and phenolphthaleïn, whereby the weight of acetic acid present can be calculated, and the difference between the amount thus found and the weight of the portion of filtrate operated on gives the weight of oil dissolved by the acetic acid in that quantity of the filtrate.[1] When examined in this manner, the solubility of mineral lubricating oil (apparently from petroleum) varied from 2.67 to 6.50 grammes for 100 grammes of glacial acetic acid, while a sample of crude rosin oil of 1.0023 specific gravity showed a solubility of 16.87 per cent. The solubility of a mixed sample does not, however, increase regularly with the proportion of rosin oil present.

Demski and Morawski (*Dingl. Polyt. Jour.*, cclviii, 82) recommend the use of acetone for the detection and rough determination of rosin oil in mineral oils. According to these chemists, rosin oils are miscible with acetone in all proportions, while mineral oils require several times their volume of acetone to effect solution. The test is applied by agitating 50 c.c. of the sample with 25 c.c. of acetone. If, on allowing the mixture to stand, it separates into two layers, 10 c.c. of the upper or acetonic layer should be removed with a pipette and evaporated, and the residual oil weighed. In the case of pure American or Galician lubricating oil the residue will weigh about 2 grammes, but only half this quantity will be obtained from Wallachian or Caucasian oil. The relative proportions of mineral and rosin oils in the residue may be deduced from its specific gravity as determined by Hager's method (Vol. I, p. 26). The proportion of rosin oil which requires to be added to the sample to render the mixture permanently miscible with half its measure of acetone is next ascertained. The beginning of complete solution is always indicated by the formation of a relatively persistent froth on shaking. It is stated that mixtures of rosin oil with

[1] The presence of resin acids in the rosin oil would alter its solubility, and also make the determination of the acetic acid inaccurate. It would be better to neutralise the greater part of the acetic acid, dilute with water, and extract the rosin oil by agitation with ether.

the lubricating oils from American and Galician petroleum are permanently soluble in half their volume of acetone if the proportion of rosin oil exceeds 35 per cent. of the mixed oil, but that complete solution is not effected in the case of Wallachian and Caucasian oils unless the rosin oil constitutes at least 50 per cent. of the mixture. Ragosine cylinder oil requires an addition of rosin oil equal to 53 per cent. of the mixture to become soluble in half its volume of acetone. The results of the test will doubtless be affected in a sensible manner by the character of the rosin oil employed.

A test for rosin oil in the presence of mineral and saponifiable oils has been based on Storch's reaction with sulphuric acid, but in its original form the test is fallacious in presence of cholesterin, &c. As modified by T. Morawski, the sample is dissolved in acetic anhydride, with the aid of gentle heat, the liquid cooled, and a few drops of sulphuric acid of 1.53 specific gravity allowed to flow down the side of the test-tube, so as not to mix with the contents. In presence of rosin oil or rosin, a violet-red coloration will be produced at the point of contact. Holde modifies the test by simply shaking up the oil with sulphuric acid of 1.53 gravity. In a subsequent paper he increases the strength of the acid to 1.624 specific gravity, which is stated to give the reaction more promptly. The different modifications of the test have been investigated by A. Grittner (*Zeits. angew. Chem.*, 1891, p. 265; abst. *Analyst*, xvi, 155), who considers the weaker acid preferable, since with the stronger, other oils are liable to give colorations which more or less obscure that due to rosin oil. For train oils containing but a small proportion of rosin oil, Morawski's method is preferable, but with dark oils Holde's is the better. Morawski's test is inapplicable to dark lubricating mineral oils. In the possible presence of resins, such as colophony or shellac, it is necessary to saponify the oil and test the unsaponifiable matter. A modification suggested by Holde (*J. S. C. I.*, vii, 526) is to agitate the oil to be tested with alcohol, and apply the test to the separated alcoholic liquid or the residue left on its evaporation. By careful procedure, very small proportions (*e. g.*, 1 per cent.) of rosin oil can be detected by the above reaction.

From experiments made in the author's laboratory, J. Thompson found the following method of operating to be the most satisfactory: About 1 cc. of the oil to be examined is placed on a porcelain crucible lid and 2 c.c. of acetic anhydride well mixed with the oil and warmed. In the case of oils not completely soluble in acetic anhydride, the mixture should be made in a test-tube, and the lower layer separated and placed on the porcelain lid. A drop or two of sulphuric acid (specific gravity 1.53) is then added to the acetic anhydride solution, when a

beautiful purple coloration will be obtained in the presence of rosin oil, rosin, &c. When the test was performed as above described on a flat or slightly concave porcelain surface, better results were obtained than by pouring the acid down the side of a test-tube.

The colorations obtained by the stannic bromide and acetic anhydride and sulphuric acid tests for rosin oil are mainly due to the hydrocarbon oils present, as is shown by the following results obtained in the author's laboratory:—

	Resin Acids.	Unsaponifiable Matter.
Stannic bromide, ...	Faint coloration on standing.	Strong purple colour.
Acetic anhydride and sulphuric acid (1.53 sp. gr.), ...	Faint purple, fading immediately.	Brilliant purple, fading in a few minutes.

Another colour-test for the detection of rosin oil in the presence of mineral oils, &c., has recently been described by G. Halphen (abst. *Analyst*, 1903, xxviii, 9), and is based on the fact that rosin oil gives an intense violet and blue coloration with a solution containing bromine and phenol, while mineral oils give only a brown colour with a slight violet fluorescence. The presence of water or alcohol interferes with the reaction. The substances causing the coloration are apparently identical with those giving the Liebermann reaction, and these can be extracted with strong alcohol, when the dry residue gives the colour with greater intensity. The test is carried out as follows: A drop of the oil to be examined is thoroughly mixed with 2 c.c. of a solution of crystallised phenol in carbon tetrachloride (1 in 2) in a porcelain crucible, .and bromine-vapour, from a flask containing bromine dissolved in carbon tetrachloride (1 in 4), allowed to fall into the crucible. The reaction is complete in from five to ten seconds. Comparison tests with samples of known composition should be made, when less than 10 per cent. of rosin oil may be detected. Chinese wood-oil gives a carmine coloration with violet or blue tinge, and marine animal oils give a carmine colour. Other oils give either much fainter or only indefinite reactions, among the latter being most vegetable oils.

For the detection of mineral oil in rosin oil, D. Holde (abst. *Analyst*,. 1902, xxvii, 14) dissolves by agitation 10 c.c. of the sample in 90 c.c. of alcohol (of 96 per cent. strength) at the ordinary temperature. Any considerable quantity of undissolved matter is stated to indicate the presence of mineral oil. After repeated solution in hot alcohol of 96 per cent., and fractional precipitation of the solution by water, the product will have a refractive-index below 1.533 if mineral oil be present.

Walker and Robertshaw (*Analyst*, 1902, xxvii, 238) state, how-

ever, that Holde's method does not admit of general application, since many rosin oils contain as much as 40 per cent. of matter insoluble in alcohol.

H. Herzfeld (abst. *Analyst*, 1903, xxviii, 42) determines the proportion of mineral oil in rosin oil by adding, drop by drop with constant shaking, 15 cc. of fuming nitric acid to 10 c.c. of the sample. The vessel in which the reaction takes place is cooled by means of an outer vessel, through which a stream of cold water circulates. The operation requires great care, since if the temperature be kept too low, the reaction is at first sluggish, but suddenly sets in with extreme violence. The products of the oxidation of rosin oil by nitric acid are soluble in the acid, and after the completion of the reaction, which requires about 20 minutes, the volume of mineral oil may be read off.

ROSIN GREASE is made by stirring together rosin oil and slaked lime. One method of preparation consists in stirring the rosin oil with about three-fourths of its weight of slaked lime made into a cream with water. The mixture rapidly solidifies, extruding the superfluous water, which is run off, and the grease is then diluted by gradually stirring in a further quantity of oil, until the desired consistency is attained. The oil used for diluting may be rosin oil, petroleum oil, or neutral coal-tar oil ("grease oil"). Rosin grease is also made by mixing dry slaked lime with rosin oil, without water, or by mixing the lime with mineral or coal-tar oil, and adding the rosin oil afterwards. Barium sulphate, gypsum, whiting, and other make-weights are also added. Cheap greases are thus prepared, which are used to lubricate the iron axles of colliery trucks and ordinary road vehicles. Rosin grease rapidly acetifies by heat and friction, and hence is not adapted for the lubrication of brass bearings.

The formation of rosin grease has been attributed by E. J. Mills to a supposed property possessed by the unsaturated hydrocarbons contained in rosin oil of combining directly with lime and other bases ("Destructive Distillation," 4th edition, 1892, p. 97). The true explanation is that crude rosin oil invariably contains a considerable percentage of resin acids (undecomposed colophony), which have distilled over with the hydrocarbons, and it is the combination of these acids with the lime which is the real cause of the formation of rosin grease. According to L. Archbutt, refined rosin oil, which has been freed from resin acids, is incapable of forming a grease with lime; while, on the other hand, the larger the percentage of resin acids contained in the crude rosin oil, the stiffer the grease which can be formed.[1]

[1] The percentage of resin acids in three samples of commercial rosin oil was determined by Archbutt by dissolving a weighed quantity of each oil

Archbutt and Deeley give the following analyses of two samples of rosin grease:

	A.		B.
Hydrocarbon oil,	87.7	per cent.	86.6
Resin,	3.7	"	7.0
Slaked lime (CaH_2O_2),	6.4	"	4.5
Water, etc. (by difference),	2.2	"	1.9
	100.0		100.0

Copal.

Copal is the so-called recently-fossilised resin of various species of *Trachylobium* and *Hymenæa* (Order, *Cæsalpinieæ*). The best resin appears to be the product of *T. Mossambicense*, generally known as *Zanzibar Copal.*[1]

Copal is one of the most important of the varnish resins. It is hard, tasteless and odourless, transparent, and of conchoidal fracture. It is almost invariably melted before being used for making varnishes, &c.

The name "copal" is applied to the resinous product of several other natural orders. Hence it is quite impossible to trace the actual resins upon which various chemists have reported, and their work consequently loses much of its value.

Tschirch and Stephan have investigated the chemistry of an authentic specimen of Zanzibar copal, which they found to contain the following compounds: 80 per cent. of *trachylolic acid*, $C_{54}H_{85}O_3(OH)(COOH)_2$; about 4 per cent. of an isomeric acid, *isotrachylolic acid;* two indifferent neutral resinous bodies, *α-copalresene* and *β-copalresene;* and about 10 per cent, of *essential oil.* The ash was only 0.12 per cent.

The different varieties of copal have been the subjects of numerous investigations by Tschirch and his collaborators, whose results are tabulated on the next page.

in ether, shaking out with soda, and weighing the resin acids recovered from the soda solution. The following results were obtained:—

Description of Rosin Oil.	Resin Acids.
A. "Pale refined,"	0.14 per cent.
B. "Medium,"	5.80 "
C. "Hard-run,"	21.30 "

The acids extracted from each sample were quite hard and brittle.

20 grammes of each of the above oils was stirred with about 45 c.c. of a cream of lime, containing about 15 grammes of slaked lime. The mixture made from sample A did not perceptibly thicken on stirring and formed no solid grease on standing. Both the other mixtures set. The hydrocarbons isolated from sample C by dissolving the oil in ether, agitating the liquid with caustic soda, and evaporating the separated ethereal layer, showed no tendency to emulsify when treated with milk of lime, even after a long period.

[1] A new source of "copal resin" has recently been found in the leaves and other parts of the tree *Dipteryx odorata.*

COMPOSITION OF COPALS.

	ZANZIBAR COPAL.	MANILA COPAL.	(New Zealand) KAURI BUSH COPAL.
Botanical Origin	(Fossil and recent) *Trachylobium* and *Hymenæa* species.	*Dammara orientalis.*	(Fossil) *Dammara Australis.*
RESIN ACIDS.			
A. Soluble in Am. Carbonate,			
a. Crystallisable,		Mancopalic, $C_8H_{12}O_2$. (M. Pt. 175°) K_1 . I_1 . $[\alpha]_D = +56°$ } 4 %	Kauric or Kaurinic, $C_{10}H_{16}O_2$. (192°) . K_1 . I_1 . $[\alpha]_D$ +51.7; 1.5 %.
b. Amorphous,		Mancopalenic, $C_8H_{14}O_2$. (100–105°) K_1 . I_1. } 4 %	
B. Insoluble in Am. Carbonate,			
a. Crystallisable,			
b. Amorphous,		Mancopalolic, $C_{10}H_{18}O_2$; 75 to 80 %.	*a*- and *β*-Kaurolic Acids, $C_{12}H_{20}O_2$. (48 to 50 %). Kaurinolic and Kauronolic Acids. (20–22 %.)
a-acid, ppted. by alcoholic lead acetate,	Trachylolic, $C_{56}H_{88}O_8$, 80% (sphærocrystals, 168°) . K_2 (probably).	(85–90°) K_1 . I_1.	(*a*-Kaurolic (81–83°) . K_1 . I_1. Kaurinolic, $C_{17}H_{34}O_2$. (128–130°). K_1 . I_1.
β-acid, not ppted. by alcoholic lead acetate,	Isotrachylolic (106°) . K_2 . 4%.	(83–88°) K_1 . I_1.	*β*-Kaurolic (85–87°) . K_1 . I_1. Kauronolic, $C_{12}H_{24}O_2$. (86–89°). K_1 . I_1.
INDIFFERENT RESINS.	*a*-copalresene (75 to 77°). $[\alpha]_D$ (in alcohol), +12.5°. *β*-copalresene. } $C_{25}H_{38}O_4$. 6 %. (Decomposes at 140° without melting.)	Mancopaloresene, $C_{20}H_{32}O$. } 12 % (80–85°).	Kauroresene, 12 %, 63 to 65° (impure).
ESSENTIAL OIL.			
A. Readily volatile with steam,	9 %.	(B. Pt. 165–170°); 6 %. Sp. gr. 0.840.	(150 to 160°); 12.5 %. Sp. gr. 0.835.
B. Tailings,		—	Small.
MINOR CONSTITUENTS. Bitter principle, alkaloid, succinic acid, colouring matter, water and impurities,	About 0.5 %.	3 %.	0.5 to 2 %.
REFERENCE.			
Original	*Arch. Pharm.*, 1896, p. 552.	*Arch. Pharm.*, 1902, p. 202.	*Arch. Pharm.*, 1901, p. 145.
Abst. *Jour. Chem. Soc.*,	1897, i, 92.	1902, i, 478.	1901, i, 398.
		Another sample of Manila copal contained no acids soluble in ammonium carbonate.	

Copal is not soluble in the usual organic solvents except to a limited extent, unless it be heated sufficiently to effect partial decomposition, and drive off a certain amount of volatile oil.

According to A. Tschirch, the following quantities of copal are dissolved by various solvents: acetone and ether, 34 per cent.; benzene, chloroform, acetic acid, and toluene, 30; amyl alcohol, 40; petroleum-ether and carbon disulphide, 10 per cent.; and alcohol, almost entirely soluble on long standing.

Lippert and Reissiger (*Zeits. angew. Chem.*, 1900, p. 1047; abst. *Analyst*, 1901, xxvi, 22) obtained the following results by the analysis of various commercial samples of copal. For the determination of the acid value, one gramme of the sample was treated with 10 cc. of chloroform, and after standing some hours, 25 cc. of alcohol was added. If the copal was not dissolved by this treatment, ether, or a mixture of alcohol and ether, was used, and when solution was complete, the liquid was titrated with semi-normal alcoholic potash, using phenolphthaleïn as indicator. The saponification-value was obtained by heating the copal with alcohol and ether (not chloroform), adding excess of standard alcoholic potash, and proceeding as usual. The ester number is the difference between the acid and saponification values. In certain cases, such as Manila copal, it probably represents lactonic bodies and not esters.

Variety of Copal.	Acid Value.	Saponification Value.	Ester Value.	Remarks.
Angola, white,	59 to 61	....	...	R. Williams[1] found acid value 57.
Angola, red.,	90	148 to 152	58 to 62	Schmidt and Erban[2] found saponification value 148.
Angostura,	48	...	...	Fine glassy yellow lumps.
Benguela, select,	61 to 62	111 to 126	50 to 64	Clear yellow balls.
Benguela, ordinary,	84 to 87	...	....	Contains dirt.
Brazil, select,	153 to 158	148 to 157	1 to 5	Splendid pale yellow balls.
Cameroon,	106 to 109	...	...	Easily soluble in alcohol.
Dammar,	33 to 35	...	...	Completely soluble in oil of turpentine.
Kauri, select,	81	...	...	Not quite transparent.
Kauri, light ordinary,	63 to 64	95 to 109	32 to 39	Williams found saponification value 64.2.
Kauri, dark,	66.5 to 70	...	...	
Madagascar,	60	...	...	Easily soluble in alcohol-chloroform.
Manila, select,	103 to 111	147 to 152	44 to 50	Hard, easily soluble in alcohol.
Manila, soluble in alcohol,	144 to 148	...	...	Soft, easily soluble in alcohol.
Sierra Leone,	78 to 82	...	...	Small light balls.
Zanzibar,	...	88 to 102	...	Characteristic "goose-skin" appearance.

[1] Williams' results will be found in detail in *Chem. News*, lviii (1888), page 224.

[2] Schmidt and Erban's results are recorded in *J. S. C. I.*, viii (1889), page 308. C. Coffignier has published further constants and solubility values for Zanzibar and Madagascar copals (*J. S. C. I.*, 1903, p. 808).

Natural copals are melted before being used in the preparation of oil varnishes, this treatment rendering them soluble in fixed and essential oils. A loss of from 10 to 25 per cent. or more of the weight of the copal by the destructive distillation takes place, with formation of gas and "copal oil" products which are of little value. To reduce the loss, Violette and also Prechtl melt the copals in closed vessels under a pressure of about 20 atmospheres. Varieties of copal and amber treated in this way are stated to dissolve well when melted with linseed oil and oil of turpentine, but the practical value of the process is disputed (see Lippert, *J. S. C. I.*, 1901, p. 1122; 1902, p. 1460).

Von Schmidt and Erban found that shelled copals from various sources were much more soluble in alcohol and oil of turpentine than the natural copals, which were insoluble in alcohol and only partly soluble in turpentine.

Mauch finds that genuine Zanzibar copal is insoluble in 80 per cent. chloral hydrate solution, whilst dammar, colophony, and Kauri and Manila copals are partly or entirely soluble.

R. A. Worstall has published some valuable constants yielded by the fossil resins (*Jour. Amer. Chem. Soc.*, 1903, xxv, 860). Unfortunately Worstall determined the "acid" value by Dieterich's indirect process. The iodine values obtained by this observer (by treating 0.2 gramme of the sample and 10 cc. of chloroform with 50 cc. of Hübl solution for 18 hours in the usual way) were as follows:—

Copal.	No. of Samples Examined.	Iodine Value. Max.	Iodine Value. Min.
Kauri,	43	170	74
Manila,	19	148	104
Pontianac,	2	142	119
Zanzibar,	2	123	115
Mozambique,	1	136	
Madagascar,	1	126	
West African,	8	143	122
Sierra Leone,	2	105	102
Brazilian,	3	134	123

Schmidt and Erban (*J. S. C. I.*, 1889, page 308) found, in the case of *melted* Angola copals, 93.6 and 25.2 for the acid and ester numbers respectively of the white variety, and 30.5 and 89.2 for the same constants of the red variety. The iodine absorption of the white Angola copal was 44.9 and 34.8 for the red variety.

Hirschsohn states that only 6.5 per cent. is extracted by petroleum-ether from good African copal, while chloroform extracts from 42 to 52 per cent., according to the variety. The same authority gives 91 as the saponification number of unmelted Zanzibar copal, the melted resin having a value as low

as 35.7. For Angola copal he gives 131 to 147.3 for the unmelted, and 110.2 to 120.3 for the melted resins.

By the dry distillation of several varieties of copal, M. Guédras (*Compt. rend.*, cxxxv, 797; abst. *J. S. C. I.*, 1902, page 1460) obtained about 8 to 15 per cent. of *oil*, soluble in each case in alcohol, ether, benzol, and carbon disulphide, but not in the terpenes. The characteristic odour of terpin in the distillate from the oil oxidised by nitric acid, and the presence of oily drops smelling of camphor, suggest that the copals contain oxidised terpenes.

ANIME RESIN is of somewhat variable and, in many cases, doubtful origin. It appears in general to be closely related to elemi and copal, and is usually the product of species of *Bursera*. Anime is frequently known in English commerce as *soft copal*, while Madagascar copal is known in France as *anime*. The so-called East and West Indian anime is the product of *Hymenea Courbaril*, and the same name has been applied to resins from various other sources.

The chemistry of anime resin is naturally but little understood. Anime appears to contain a large amount of essential oil, which, according to Paoli, is sometimes present to the extent of 24 per cent.

A sample of anime examined by E. Dieterich contained 54.3 per cent. of resin soluble in cold alcohol, and 43 per cent. of resin soluble in hot (but insoluble in cold) alcohol.

The analytical figures which have been recorded for this resin will be found on page 150.

Dammar Resin.

The chief variety of this resin which occurs in commerce is in all probability the product of a variety of *Hopea*, one of the *Dipterocarpeæ;* but other plants are said to have produced much of the resin, such as species of *Vatica*, *Dryobalanops*, *Doona*, and *Vateria*.

Dammar resin is a hard, pulverisable substance melting at about 180° C., partially soluble in methyl and ethyl alcohols, ether, acetone, and glacial acetic acid; almost entirely in petroleum-ether; and completely soluble in benzol, chloroform, carbon disulphide, and oil of turpentine.

The constituents of dammar resin which have so far been identified (G. Glimman, *Archiv der Pharm.*, 1896, p. 584) are as follows: dammarolic acid, $C_{54}H_{77}O_8(COOH)_2$, which is present to the extent of 23 per cent.; α-dammarresene, $C_{11}H_{17}O$ (40 per cent., soluble in alcohol); β-dammarresene, $C_{31}H_{52}O$, (22.5 per cent., insoluble in alcohol); ethereal oil and a bitter substance, 0.5; water, 2.5; ash, 3.5; and undefined impurities, 8 per cent.

B. Graf (*Archiv der Pharm.*, xxvii, p. 97) examined five samples of East Indian Dammar, and found about one per cent. of a free dibasic acid having the formula $C_{18}H_{33}O_3$. Of the other portion of the resin, 40 per cent. was insoluble, and 60 per cent. soluble, in alcohol. The soluble portion was described as melting at 61°, and having the formnla $C_{20}H_{42}O_2$. The insoluble portion contained oxygen and melted at 144° to 145°. No hydrocarbon could be detected.

E. Hirschsohn examined a large number of samples of dammar and found that, with the exception of *Dammar marmoratum*, all the specimens yielded from 73 to 88 per cent. of extract to petroleum-ether, and from 57 to 87 per cent. to alcohol of 85 per cent. strength.

E. Hirschsohn (*Zeits. anal. Chem.*, 1898, page 456) states that 5 per cent. of colophony can be detected in dammar resin by digesting the sample for half an hour with solution of ammonia (sp. gravity, 0.960), and acidifying the filtered liquid with acetic acid. In the presence of colophony, a precipitate of resin acids is formed, whereas pure dammar yields a faint opalescence, since only traces of the acids of dammar resin are extracted by ammonia.

The analytical figures for this resin will be found in the table on page 150. R. A. Worstall found that 11 samples had iodine absorptions (Hübl) after 18 hours, ranging from 103 to 124.

Oil of dammar resin has a golden yellow colour and a bitter taste. According to H. Haensel, it has a specific gravity at 21° of 0.9352. It is optically inactive and boils between 205° and 265° C. Sixty per cent. of the oil distils below 240°, this fraction having a specific gravity of 0.9175. It is soluble in most organic solvents.

Dragon's Blood.

The chief variety of dragon's blood is the "Palm Dragon's Blood," from *Dæmonorops Draco*.

In this variety, Tschirch and K. Dieterich found about 18 per cent. of insoluble plant-substances; 2.5 per cent. of *dracoalban*, $C_{20}H_{40}O_4$, obtained by the addition of alcohol to the ethereal solution of the sample; about 14 per cent. of *dracoresene*, $C_{26}H_{44}O_2$; and a red amorphous powder, which after purification melts at 72° C., obtained by evaporating the filtrate from the dracoalban to dryness and extracting the residue with petroleum-ether. This last body appears to be a mixture of the benzoic and benzoyl-acetic esters of an alcohol, *dracoresinotannol*, $C_8H_{10}O_2$. Socotra Dragon's Blood, from *Dracæna cinnabari*, a variety not used to any considerable extent, appears to contain esters of both benzoic and cinnamic acids, but no dracoalban.

Dragon's blood is used to a considerable extent in the preparation of coloured varnishes or stains. It is the essential ingredient of the so-called "mahogany" stains.

Dragon's blood has a deep-brown colour externally, but they fracture and streak a bright red. The massive variety is frequently adulterated with colophony, which raises the acid value and saponification-number. In addition to colophony, oxide of iron, Armenian bole, red sanders' wood, and various gums are said to have been used as adulterants.

According to K. Dieterich, dragon's blood (freed from plant-residue) is easily soluble in alcohol and ether, but only partially soluble in benzene, chloroform, acetic ether, petroleum-ether, and carbon disulphide.

Gregor and Bamberger found the methoxyl-numbers of three samples of dragon's blood to be 27.6, 25.3 and 33.8. R. Williams found a good commercial sample to contain 9.34 per cent. of water and 3.6 per cent. of ash. K. Dieterich found 8.3 per cent. of ash. The acetyl-number of palm dragon's blood was found by K. Dieterich to be about 140.

The following test for distinguishing palm dragon's blood from other varieties has been proposed by K. Dieterich (*Analysis of Resins*, &c., page 154): 10 grammes of powdered dragon's blood should be extracted with 50 cc. of hot ether, filtered from woody-fibre and other insoluble matter, the solution concentrated to about 30 cc., and the whole then poured into 50 cc. of cold absolute alcohol. After standing for one hour, a white flocculent precipitate of dracoalban, soluble in most organic solvents but insoluble in alcohol, will be formed if palm dragon's blood be present. Other varieties of the resin are said not to contain this resene. A sample of palm dragon's blood adulterated with colophony, &c., will only respond very slowly to this test.

Guaiacum.

This resin is the product of the stem of *Guaiacum officinale* and *G. sanctum* of tropical America.

Guaiacum occurs in rounded tears and in masses of a green or brownish-green colour. It is a glassy, brittle solid, having a somewhat reddish fracture when fresh, but which darkens to green. Its odour and taste are very slight, but on chewing the resin a burning sensation is imparted to the throat. Guaiacum melts at about 85°. It is used to a considerable extent in medicine. The mass variety varies greatly in quality, and the commoner kind frequently contains a considerable quantity of woody fibre.

Apart from this impurity, which may be regarded as an adul-

teration when present in excessive amount, guaiacum sometimes contains an admixture of colophony, and is also said to be mixed abroad with another species of resin unknown in commerce.

According to Döbner and Lücker (*Archiv der Pharm.*, 1896, ccxxxiv, p. 590; abst. *J. C. S.*, lxxii, i, 165, 166), guaiacum contains about 11 per cent. of *guaiaretic acid* (guaiacum resin), $C_{20}H_{23}O_3(OH)$, crystallising in white lustrous laminæ and melting at 86°; 50 per cent. of *guaiaconic acid*, $C_{30}H_{22}O_3(OH)_2$, a white amorphous powder melting at 75° and soluble in ether; 12 per cent. of *guaiacic acid*,[1] $C_{21}H_{19}O_4(OH)_3$ (the *β-resin* of Hadelich), insoluble in ether; a yellow crystalline body, "guaiacum yellow," $C_{20}H_{20}O_7$, melting at 115° and soluble in strong sulphuric acid with deep blue coloration; about 10 per cent. of gum; 2 per cent. of ash; and undefined matters and loss.

Numerous oxidising agents produce a blue colour when brought into contact with tincture of guaiacum, and this property is the basis of several useful reactions, as, for instance, in detecting the presence of blood (Vol. IV). The coloration is due to the action of oxygen upon guaiaconic acid, the resulting body probably having the formula $C_{20}H_{20}O_6$. Döbner recommends that the pure acid itself, and not the mixture of acids obtained from a tincture of guaiacum, should be used in such tests.

The proportion of alcohol-soluble matters and of ash in guaiacum are the most important factors in its examination. Ward found the ash in three samples to range from 3 to 6.8 per cent., the matter soluble in alcohol from 87 to 96 per cent., and the matter soluble in water from 3 to 4.7 per cent. John Evans found the matter soluble in alcohol in 6 samples to range from 90.0 to 98.5 per cent., the amount of ash in the insoluble matter being very variable, and ranging from 11.5 to 56.2 per cent.

[1] The chemistry of guaiacum is of especial interest on account of the synthetic experiments of Döbner, who succeeded in obtaining resin-acids closely resembling those of guaiacum. By the condensation of tiglic aldehyde, guaiacol, and cresol, Döbner obtained a brown resin having the composition $C_{20}H_{24}O_4$, which is therefore isomeric with guaiaretic acid. From a study of the reaction in which it is formed, the constitution of the synthetic product is stated to be:—

$$CH(CH_3):C(CH_3).CH(C_6H_2.CH_3.OCH_3.OH).C_6H_3(OCH_3).OH.$$

In a similar way, by condensing tiglic aldehyde with guaiacol and the dimethyl-ether of pyrogallol, an acid isomeric with guaiaconic acid was obtained, and by using only tiglic aldehyde and the dimethyl-ether of pyrogallol, an acid having the formula $C_{21}H_{26}O_6$ was obtained. These results have strengthened the hypothesis that many of the resins are formed in nature by the condensation of bodies of aldehydic and phenolic character rather than by the oxidation of terpenes.

The following figures for guaiacum have been recorded:—

Observer.	Acid-number.	After Acetylation.	
		Acid-value.	Ester-value.
A. Kremel, ...	23 to 44		
K. Dieterich, ...	....	Mass Variety, 46 to 53 Purified by Alcohol 13.6 to 13.9	122 to 139 149 to 150

The acid values after acetylation are widely different in the case of the mass variety and of the purified guaiacum, but no explanation of the discrepancy is offered by Dieterich. Guaiacum contains mere traces of esters only.

Rabenau found from 54 to 74 per cent. of guaiacum to be soluble in ether. Very small quantities of guaiacum are soluble in petroleum-ether, up to about 4.0 per cent. after drying the residue at 120° C. The methoxyl-number of guaiacum ranges from 74 to 84 (Gregor and Bamberger).

For the detection of colophony in guaiacum, the Storch-Morawski reaction may be employed (see Colophony). Hager states that this adulterant may be detected by adding excess of caustic potash solution to an alcoholic solution of guaiacum. An insoluble resin-soap will be precipitated in the presence of colophony. The potassium salt of guaiaretic acid is, however, precipitated from guaiacum by this method (Döbner).

Hirschsohn states that the presence of either colophony or of a foreign species of guaiacum, such as the so-called Peruvian guaiacum (*Guaiacum peruvianum odoriferum*), may be detected by adding a solution of bromine to a chloroformic solution of guaiacum. Pure guaiacum yields a blue colour, while an adulterated sample will give a red coloration.

Mastic.

Mastic is the product of *Pistacia lentiscus*, one of the *Anacardiaceæ*. It occurs as small round or ovoid grains of a pale yellowish colour, which are fairly soluble in many of the organic solvents.

The chemistry of mastic is very little understood, but Flückiger isolated from it two per cent. of an essential oil, which consisted chiefly of a slightly dextro-rotatory terpene. Tschirch and Reutter (abst. *J. C. S.*, 1904, i, 333) found Chios mastic (acid number 59 and saponification number 82.5) to contain:—α- and β-masticic acids, 4 per cent.; masticolic acid, 0.5; masticonic acids, α, 20; β, 18; mastico-resenes, α, 30; β, 20 per cent.; essential oil,

2; bitter-substance, impurities, etc., 5.5 per cent. (See also tables on pp. 145 and 146.)

Mastic is sometimes adulterated, especially when in powder, with sandarac, colophony, and other pine resins. The much higher acid-numbers of these adulterants will, however, serve to indicate their presence. The iodine-absorption of mastic resin is high, usually about 180 to 190 (Hübl; 12 hrs.).

The following figures have been recorded for genuine samples of mastic:—

	A. Kremel.	R. Williams.	Von Schmidt and Erban.
Acid number, ...	61.8; 70.9 67.2 (E. Dieterich).	50.04; 56.0	64.0
Ester number, ...	....	23.00; 23.10	29.0
Ash, per cent., ...	....	0.21; 0.14	....
Water, per cent., ..	....	0.97; 1.46	....

The U.S. Pharmacopœia (8th Rev.) requires for mastic an acid number of not less than 65.

Mastic is completely soluble in 80 per cent. chloral hydrate solution, and according to von Schmidt and Erban is partially soluble in alcohol, methyl alcohol, acetone, acetic acid, chloroform, and oil of turpentine; slightly soluble in carbon disulphide; completely soluble in ether, amyl alcohol, and benzol, and insoluble in petroleum-ether.

Sandarac.

This resin is the natural exudation from *Callitris quadrivalvis* (*Coniferæ*) and allied species. Occasionally Australian sandarac, known as "pine-gum" or "white pine resin," is found on the market. Sandarac is used in certain varnishes and is known in commerce as *gum juniper*.

The constituents of sandarac are not definitely known. It appears to consist substantially of two acids[1] and an essential oil, which is stated by Henry to contain dextro-pinene and a diterpene boiling at 265° C.

[1] The composition of the resin acids of sandarac is at present the subject of conflicting results. Tschirch and Balzer (*Archiv der Pharm.*, ccxxxiv, 291) state that two acids, named by them sandaracolic acid and callitrolic acid, are present. T. A. Henry, however (*Jour. Chem. Soc.*, 1901, lxxix, 1144), alleges that these results are of doubtful value, owing to the frequent occurrence of arithmetical mistakes and incorrect formulæ throughout Tschirch and Balzer's paper. Henry found the resin-acids to contain *inactive pimaric acid*, $C_{20}H_{30}O_2$, and an acid for which he retains the name *callitrolic acid*, $C_{80}H_{48}O_5$, and which is said to be identical with the chief constituent of Tschirch and Balzer's acid of this name.

Sandarac is sometimes adulterated with colophony and possibly also with some variety of cheap dammar. The following analytical characters have been recorded:—

Observers.	Moisture; Per Cent.	Ash; Per Cent.	Acid Number.	Acetylated Resin.	
				Acid Number.	Ester Number.
E. Dieterich,	...	...	97 to 123	...	...
K. Dieterich,	...	...	90 to 110	166 to 170	74 to 82
A. Kremel,	...	...	144	...	...
Von Schmidt and Erban,	...	...	140	140	...
R. Williams,	0.04; 0.17	1.9; 1.4	154; 146	...	...

According to Flückiger and von Schmidt and Erban, sandarac is completely soluble in alcohol, ether, amyl alcohol, and acetone; partially soluble in methyl alcohol, acetic acid, and chloroform; and practically insoluble in benzene or carbon disulphide. Hirschsohn found from 7 to 8 per cent. of sandarac to be soluble in petroleum-ether, and Mauch about 5 per cent. soluble in 60 per cent. chloral hydrate solution.

Shellac.

Shellac is the secretion of the lac insect, *Tachardia Lacca* (*Coccidæ*), on a large number of widely different plants, such as *Betua frondosa* and *Ficus religiosa*, and on certain other trees specially grown for the insect.[1]

Crude "stick lac" contains much impurity in the way of dirt and woody fibre, whilst the crushed and washed lac, known as "seed-lac," is correspondingly purer. The purified resin is the form in which most of the lac is sold, and is then known as "shellac." With insignificant exceptions all the "shellac" of commerce is manufactured in or about Calcutta, but a large amount of "button lac" is made both here and in Germany. It is almost invariably a mixture of shellac and rosin.

Shellac is used very largely in various industries, notably for the preparation of a certain class of polishes and varnishes, and for the stiffening of hats and certain textile materials.

Shellac is adulterated to a very great extent with rosin. The adulteration takes place both abroad and at home. Numerous grades are recognised both of the pure and the adulterated forms. The "fine orange," which varies from a pale orange to a lemon-yellow colour, and the "second orange" grade of shellac, the latter being usually described as of "**TN** in a diamond"

[1] An important paper on the lac industry of India, by Sir George Watt, will be found in the *Pharm. Journ.*, 1905, ii, 646.

standard, should be and generally are pure; but in times of scarcity, the "second orange" quality is very often adulterated with *1 to 5 per cent. of rosin.* Numerous other grades follow these, down to samples of very bad colour. Some of the dirty yellow shellac of commerce is arsenical, being coloured with a small quantity of *orpiment* (As_2S_3). "Garnet lac" is of a very fine, deep colour, and is invariably a mixture of shellac with rosin, usually about 10 to 12 per cent. The brand known as "A. C.," in a diamond, commands a high price, and occurs in thick plates and masses, instead of in the thin flakes usually characteristic of shellac. "Button lac," a form in considerable demand for certain purposes, is (with the exception of very few brands, imported in limited quantities) almost invariably adulterated.[1] *"Pitch" is stated to be sometimes used as an adulterant of* shellac.

The chemistry of shellac has been but incompletely studied, though a few well-defined constituents have been recognised. In addition to accidental impurities, such as water (up to 4 per cent.) and small quantities of sand, woody fibre, &c., shellac contains *wax*[2] in proportions varying from traces up to about 6 per cent. There is also usually from 2 to 6 per cent. of laccin pigment present, and a small quantity of *laccainic acid*, $C_{16}H_{12}O_8$, which forms an important constituent of lac-dye, and is a body closely allied to the colouring-matter of cochineal. The resinous *matter of shellac ranges from 75 to 85 per cent.*, and was prepared by A. Tschirch by exhausting crushed shellac under a reflux condenser with petroleum-ether to remove the wax and then repeatedly treating the dried residue with warm water until the liquid was no longer coloured, an additional 6.5 per cent. being thus removed. Of the resinous matter thus purified 35 per cent. was dissolved by ether, and consisted of traces of higher fatty acids, a yellow colouring-matter called *erythrolaccin*, $C_{15}H_{10}O_5 + H_2O$ (apparently a hydroxy-methylanthraquinone), a small quantity of a crystalline odoriferous substance, and bodies apparently of the nature of *resenes*. The 65 per cent. of shellac-resin *not dissolved by ether consisted* chiefly of the aleuritic ester of a very unstable *resinotannol*.[3]

[1] It is *stated on reliable authority that not* more than about 1400 chests of pure button-lac, absolutely free from added rosin, are imported into Great Britain annually.

[2] Shellac wax melts at 59° C., and consists of a mixture of equal parts of free alcohols (chiefly myricyl and ceryl alcohols) and of the stearic, palmitic, and oleic esters of these alcohols (Benedikt and Ulzer).

[3] It has been pointed out by Ulzer and Defris that shellac resin-acids behave quite differently to the resin-acids of colophony in Gladding's or Twitchell's process, and that the former appear to be more nearly related to the fatty acids than to the resin-acids of colophony. (See Vol. II, Pt. i, and *J. S. C. I.*, *1897, page 364.*)

Aleuritic acid itself, $C_{13}H_{26}O_4$, crystallises from aqueous alcohol in rhombic leaflets, or from water or chloroform, in needles melting at 101.5°.

Tschirch states that shellac-resin is almost entirely soluble in methyl and ethyl alcohols, acetic acid, alkalies, and solution of borax; only partially soluble in ether, ethyl acetate, chloroform, acetone, and carbon disulphide; and almost insoluble in benzene, toluene, and petroleum-ether.

Von Schmidt and Erban find shellac to be soluble in methyl, ethyl, and amyl alcohols, and in glacial acetic acid; but insoluble or nearly so in ether, acetone, petroleum-ether, carbon disulphide, and oil of turpentine, and only partially soluble in chloroform.

According to Mauch, on treating shellac with an 80 per cent. aqueous solution of chloral hydrate it first swells up and then dissolves almost entirely.

On treating shellac previously dried at 120° C. with petroleum-spirit, Hirschsohn found from 0.4 to 6.3 per cent. to pass into solution. These figures probably represent the proportions of wax present in the samples examined.

The ready solubility of shellac in hot aqueous solutions of potassium and sodium carbonates, caustic alkalies, and borax is well known, and this property is utilised in several ways. On the one hand, it is made use of in the preparation of the so-called water varnishes employed in the finishing of leather, and, on the other hand, for the production of bleached shellac, and of shellac soluble to a clear solution in alcohol. The shellac remains unchanged in these alkaline solutions, and dries to a hard coat. It can be precipitated from the solution by an acid.

Benedict and Erlich have observed that shellac is largely converted by dilute alkalies into a balsam-like mass, described by them as "*liquid shellac.*" This is prepared by boiling 10 parts of shellac (previously freed from wax) with a solution of 3 parts of caustic soda in 20 of water, acidulating the cooled mass with sulphuric acid, and extracting with ether. The ether is distilled, the residue (amounting to about 70 per cent. of the wax-free resin) consisting of the "liquid shellac." The product is probably little more than shellac resin hydrolysed, and containing a considerable proportion of water (Parry). By mixing liquid and ordinary shellac, plastic masses of any degree of softness can be obtained.

Shellac is an article of considerable value, and its price is very variable. Hence it is extensively adulterated, the usual admixture being common rosin. The presence of this adulterant may be detected by the ordinary colour-tests for colophony, but these give only the roughest indication of the proportion present. E. J. Parry finds that the Storch-Morawski reaction

(page 177) will reveal the presence of rosin when present to the extent of 8 per cent. or more.

For the detection of colophony in shellac, E. J. Parry dissolves the sample in a little alcohol and pours the solution into water. The impalpable powder is collected on a filter-paper, dried, and then rubbed for some time with petroleum-ether. The filtered liquid is next shaken with a little water containing a *trace of copper acetate*, when the petroleum-ether will be coloured emerald-green if rosin be present, but in its absence will be quite colourless. As little as 5 per cent. of colopbony may be detected by this test, which is recommended by J. C. Umney as being most satisfactory.

The specific gravity of a sample of shellac has been suggested as affording an indication of the proportion of rosin present, but the densities of the two resins are too variable and too nearly alike to render the test of value. A determination of the proportion of the previously dried sample dissolved by petroleum spirit is a useful qualitative test, but the results are misleading, as the solvent acts very differently on a mixture of the two resins melted together and subsequently powdered from what it does on a sample prepared by mixing the previously-powdered resins in known proportions.

E. J. Parry has pointed out (*Chem. and Druggist*, Oct. 26, 1901, page 689; 1902, page 670; Jan. 31, 1903, page 175; 1905, page 556) that the determination of the iodine-absorption of the sample by Hübl's process affords the most ready and accurate means of determiming the proportion of colophony in adulterated shellac, the iodine-figure for shellac being remarkably low, while that for the adulterant is exceptionally high. The iodine solution should be present in large excess (100 per cent.) and should be allowed to react for 18 hours in the dark. If the deduction from the result be confirmed by determinations of the acid and ester-numbers of the sample, a very fair approximation to the true amount of colophony present can be obtained. Parry gives the following figures obtained from the analysis of a large number of absolutely pure samples:—

	Shellac.	Colophony.
Iodine Absorption (per cent.), ...	7.5 to 11 (average 9)[1]	125 (average).
Acid-number, ...	55 to 65 (average 60)	165 (average).
Ester-number, ...	150 (average)	0 to 6.[2]

[1] Parry states that the iodine-absorption of arsenical lac sometimes reaches 14 per cent. J. C. Umney prefers the value 10 as being the average iodine absorption (Hübl) of shellac, while agreeing with Parry's figure 125 as the average iodine value for colophony.

[2] Beckurts and Brüche found the ester number of colophony to vary from 0.0 to 12 (in red samples). Von Schmidt and Erhan obtained 8.2 and 17.5 for ordinary rosin, and 7.0 and 24.4 for the refined substance.

Figures varying from 20 to 30 for the iodine-absorption of shellac have been repeatedly published, but Parry is strongly of opinion that the great majority of these results were obtained from adulterated samples.

A. C. Langmuir (*J. S. C. I.*, 1905, p. 12) advocates the use of Wijs' solution in determining the iodine value of shellac as a means of estimating the proportion of rosin present, and finds the average values 18 (for shellac) and 224 (for rosin) after one hour's action at 21° to 24° C. Although the action is quicker than in the case of Hübl's solution, yet the variation in the Wijs' iodine values of rosin samples is so much greater that the Hübl solution is preferable, a more accurate determination of rosin in shellac being obtained by its use. Langmuir's value 224 is probably too low an average for the Wijs iodine value of rosin.

The end-reaction in the determination of the acid value of shellac is often very difficult to see, especially in the case of dark-coloured samples. For this reason, Parry recommends running in an excess of alkali and titrating back the excess with acid. The acid and ester values of shellac are useful as checks on the iodine-absorption results, but owing to the limits of these values for shellac and colophony being nearer than in the case of their iodine numbers, they do not afford so useful a basis for a calculation of the rosin present as the latter figure.

The following process for the determination of colophony in shellac, based on the methods of Gladding and Twitchell for the separation of fatty and resin acids, is recommended by E. J. Parry: About 0.5 gramme of the sample is dissolved in the smallest possible quantity of alcohol and the solution cautiously treated with alcoholic potash till it is just neutral to phenolphthaleïn. This solution, containing the potash salts of the shellac and resin acids, together with the neutral constituents of the shellac, is poured into about 100 cc. of water contained in a separator, and about 0.5 gramme of silver nitrate, dissolved in a little water, added. The acids are precipitated as silver salts, and on shaking the liquid twice with ether, the silver salts of the resin-acids of colophony are completely dissolved, while the silver compounds of the shellac acids remain insoluble. The ethereal solution is filtered, repeatedly agitated with water to remove silver nitrate, dilute hydrochloric acid added, and the liquid well shaken. The silver salts are decomposed, silver chloride being precipitated, and the resin acids recovered by evaporating the washed ethereal solution to dryness. The purity of the resin acids thus obtained may be verified by their iodine-absorption. The above process only gives approximate results, the chief source of error being the slight solubility of a portion of the neutral constituents of shellac in ether, so that the results are rather higher than the truth.

Except in cases where the proportion of colophony is very small, the process yields useful confirmatory results.

White or Bleached Shellac occurs in twisted masses resembling "peppermint rock." It contains aleuritic acid, but no wax. It is prepared by dissolving ordinary shellac in an alkaline solution, preferably sodium carbonate, and treating the liquid with chlorinated lime. Hydrochloric or sulphuric acid is then added, when the shellac is precipitated in a nearly colourless condition. The bleaching is due to the destruction or alteration of the erythrolaccin (page 191). Bleached shellac, even when quite hard, usually contains a considerable proportion of water. It is not entirely soluble in alcohol, a substance resembling "lack-stoff" being left as a residue. It is said to lose its solubility in alcohol very greatly by keeping, unless it is stored under water. In epichlorhydrin, bleached shellac is but sparingly soluble, and not much more so when the liquid is warmed; but in warm dichlorhydrin it is almost completely soluble. According to Tschirch, bleached shellac contains chlorine, so that the iodine-absorption is materially modified. Rosin is usually added to this variety of shellac, notwithstanding the high estimation in which it is commonly held, but snch adulteration is easy to detect, and an approximate determination can be made.

OLEO-RESINS. TURPENTINES. BALSAMS.

The *oleo-resins* are a class of resinous exudations from plants, excreted naturally or obtained by tapping the trees. They consist essentially of mixtures of acid resins, resenes, and volatile oils, and rarely contain esters.

The name *turpentine* ought, strictly speaking, to be limited in its application to the oleo-resinous exudations from coniferous trees (e. g., *Pinus, Abies, Juniperus*). It is, however, often applied to the spirit or essential oil, (*e. g.*, oil of turpentine) obtained by distilling the crude turpentine, when the non-volatile resin is obtained as a secondary product.

Balsams are, correctly speaking, such of the oleo-resinous exudations of plants as contain benzoic or cinnamic acid, and yield cinnamate or benzoate of methyl or ethyl by dry distillation. They are liquid, more or less viscous, and yield essential oils on distillation with water. The term balsam is misapplied to "Canada balsam" and "copaiba balsam," which are true turpentines not containing or yielding benzoic or cinnamic acid; whilst "dragon's-blood" would be more properly classed among the resins.

The turpentines are viscous, honey-like liquids, or soft or

brittle solids. Their odour is generally terebinthinate, but sometimes agreeably aromatic, and their taste varies from bitter, nauseous, and acid, to a pleasant aromatic flavour. The oleo-resins are not sensibly soluble in water, though some yield traces of formic and probably succinic acid to that solvent, and, according to Tschirch, an alkaloidal body.

The description of the minute and often inappreciable differences between the various oleo-resins known in commerce as turpentines and balsams belongs rather to a work on pharmacy or materia medica than to one on chemical analysis. As their recognition and examination are rarely required, it is unnecessary to describe the majority of them in detail.[1]

Common Turpentine.

Common or American turpentine is the oleo-resin collected from pine-trees growing in the Carolinas and other of the Southern United States. The greater part of American turpentine is obtained from the "longleaf" pine (*Pinus Australis*). The "loblolly" or "oldfield" pine (*P. tæda*), the "pitch" pine (*P. rigida*), and the "swamp" or Cuban pine (*P. Cubensis*) supply comparatively small quantities only. The crude turpentine is collected in pockets cut in the trees a few feet from the ground. The flow of the first year, called *virgin dip*, is the best, and one barrel yields on distillation about six gallons of essential oil and a residue known as *window-glass rosin*. *Yellow dip*, the product of the second and subsequent years, yields about four gallons of oil per barrel, and furnishes the medium qualities of rosin. The turpentine which hardens on the trees is called *scrapes*.[2] On distillation, it yields about two gallons of oil per barrel, and leaves a very dark-coloured (nearly black) rosin.

The essential oil obtained by the distillation of American turpentine constitutes the oil of turpentine of commerce (which see). The resinous residue is known as colophony (page 157).

American turpentine was formerly distilled dry, but now an addition of water is usually made, so that the oil may pass over in a current of steam, and over-heating be avoided. The stills, which are of copper, hold from eight to fifty barrels. The

[1] Much information on the origin, methods of obtaining, and characters of the turpentines and balsams will be found in Hanbury and Flückiger's *Pharmacographia*, and in Watt's *Dictionary of Chemistry*, vol. i, p. 491 *et seq.*, and viii, 1743. A most exhaustive series of articles by Julius Morel were published in the *Pharmaceutical Journal* [3], vol. viii, pp. 21, 81, 281, 342, 542, 725, 886, 981, 1024; and vol. ix, pp. 673 and 714.

[2] *Thus Americanum*, B. P., or common *Frankincense*, is the concrete oleo-resin scraped from the trunks of *Pinus palustris* and *P. tæda*. The terebinthina (white turpentine) of the U. S. Pharmacopœia is the same substance. The name "frankincense" is also applied to the resin of olibanum.

vapour is condensed in a worm surrounded with cold water, and the distillate flows into a tank, where the oil collects on the surface. The resin which remains in the still is run off while still fluid and constitutes the common *rosin* or *colophony* of commerce.

Bordeaux or French Turpentine.

This product, also called *Gallipot* or *Barras*, is mostly the product of *Pinus maritima*, but smaller quantities are obtained from the *pin franc* or frankincense pine. In physical characters it closely resembles American turpentine, but on distillation yields a lævo-rotatory oil and a resin which contains *pimaric acid* (page 159).

Russian turpentine is the oleo-resinous exudation from the Scotch fir, *Pinus sylvestris;* German, from the same species or from *P. rotundata;* Austrian, from *P. Laricio;* Hungarian, from *P. pumilio;* Strassburg or Alsace turpentine is the product of the silver fir, *Pinus picea* or *pectinata* (otherwise, *Abies excelsa*). It has an agreeable odour, resembling that of lemon.

The following analytical data have been recorded for common turpentines.

	ACID-VALUE.	ESTER-VALUE.	SAPON.-VALUE.
E. Dieterich:			
American,	112–139	9.8–32.5	140–161
French,	105–141	2.8–9.8	109–149
Carpathian (*P. Cembra*),	117–119	56–60	167–179
P. Sylvestris,	129–145	35–39	167–180
K. Dieterich,	107–116	4.1–20	115–134
Dietze: French,	120–120.4	1.8–3.0	121–123

More constant and reliable results would be obtained by first driving off the essential oil in a current of steam, and determining the acid- and saponification-numbers of the residue.

Venice Turpentine or Larch Turpentine.

This product is the oleo-resin from *Larix Europæa* or *Pinus larix*. It is a viscous liquid of a yellowish or greenish-yellow colour. It has a characteristic pleasant smell and bitter taste, attributed by Flückiger to the presence of a glucosidal principle. The resin of larch turpentine is stated to be dextro-rotatory, while the oil exhibits lævo-rotation.

The chemical composition of larch turpentine has been recently studied by Tschirch (see page 200).

The following analytical data have been recorded for Venice or larch *turpentine*:—

	Acid-value.	Ester-value.	Sapon.-value.	Iodine Number.
A. Kremel,	68–70			
Von Schmidt and Erban,	68	30	97	—
Von Italie,	70	50	120	—
E. Dieterich,	64–77	35–56	108–133	—
K. Dieterich,	67–69	46–55	115–128	—
A. Rudling,	74	48	122	148

K. Dieterich has also recorded the following acetyl-values for larch and ordinary turpentine:—

	Larch Turpentine.	Common Turpentine.
Acetyl-acid-value,	70–72	124–126
" Ester-value,	109–119	62–94
" Saponification-value,	179–191	188–217

A factitious article, to which the name "Venice turpentine" is improperly applied, is made by mixing rosin, rosin oil, and oil of turpentine. It is employed in the manufacture of varnish and sealing-wax. Such an article would necessarily give variable analytical figures, dependent on the proportions of its constituents, but a mixture of three substances mentioned above would have a high acid-number, a very low ester-number, and would contain a considerable proportion of unsaponifiable matter. Six samples examined by G. Fabris gave distillates below 250° C. varying from 6.5 to 13 per cent.; acid-values from 105 to 114; and saponification-values from 113 to 119. Genuine larch turpentine is said to yield not less than 15 per cent. of essential oil.

A factitious Venice turpentine analysed by A. Rudling had an acid-number of 103; a saponification-value of 117.6; and an iodine-number of 109.8.

A sample of so-called "Venice turpentine" examined in the author's laboratory by A. R. Tankard gave the following results: Acid-number, 80.1; ester-number, 7.73; saponification-number, 87.8; unsaponifiable matter (liquid, and gave reactions of rosin oil), 51.92 per cent.; essential oil (volatile with steam), 3.0 per cent.; and optical activity of 10 per cent. alcoholic solution of residual resin, + 1.75° per 100 mm. From these results it is

evident that the sample contained a considerable proportion of colophony and rosin oil.

To detect rosin oil, G. Fabris dissolves 5 grammes of the sample in 20 cc. of 95 per cent. alcohol, and adds a 10 per cent. solution of caustic potash till the mixture is alkaline to phenolphthaleïn. Venice turpentine thus treated yields a perfectly clear solution, whereas the factitious turpentine containing rosin oil becomes turbid, and on standing oily drops separate.

L. E. Andés recommends as a useful adjunct to the analytical values, and the observation of the odour, inflammability, and solubility in 90 per cent. alcohol, the following test, suggested by Hirschsohn, who has observed that ordinary turpentine, on treatment with five measures of ammonia solution (sp. gr. 0.96), gradually yields a milky emulsion, whilst in the case of larch turpentine the liquid remains clear. When the lower layer of larch *turpentine is stirred it is gradually transformed into a semi-solid*, opaque substance, whilst the supernatant liquid becomes slightly turbid. Ordinary turpentine, however, is immediately distributed, and the milky emulsion rapidly solidifies to a gelatinous mass. In the case of a mixture of the two in equal parts, the substance is distributed throughout the ammonia, and a solid mass, which clears on heating, is obtained in about five minutes. When the mixture only contains about 20 per cent. of ordinary turpentine, the milky emulsion becomes clear on heating the tube in boiling water, but no solidification occurs. Comparative tests with genuine larch turpentine may serve to detect smaller quantities. When 1 part of the sample is shaken with 30 parts of 80 per cent. alcohol, a clear and permanent solution is obtained with larch turpentine, whilst in the case of ordinary turpentine about half of the substance soon separates out.

Canada Balsam.

This product, also known as Balsam of fir and Balsam of Gilead, is the oleo-resinous exudation of the so-called balsam-fir, *Abies balsamea*, and allied species. It is used to a limited extent in medicine, in the preparation of flexible collodion, and for mounting microscopic preparations.

Canada balsam is dextro-rotatory ($+1°$ to $+4°$), but on steam-distillation yields from 15 to 25 per cent. of a lævo-rotatory essential oil, boiling about 160° and consisting almost entirely of terpenes. (See also *Pharm. Jour.*, 1900, ii, 489.) Canada balsam yields a turbid solution with 5 volumes of 90 per cent. alcohol or of absolute alcohol. It has a specific gravity of about 0.990, and a refractive-index of 1.520 at 20° C.

The usual adulterants of Canada balsam are colophony and

COMPOSITION OF CONIFEROUS RESINS.

	STRASSBURG.	BORDEAUX.	VENICE.	FINLAND.	JURA.	CANADA.	TURPENTINE from:—	WHITE PITCH. (Russian "Beljivar.")
Botanical Origin, ...	White Fir, *Abies pectinata.*	*Pinus maritima.*	Larch, *Larix decidua.*	*Pinus Sylvestris.*	*Picea vulgaris.*[1]	*Abies Canadensis.*	*Pinus palustris.*	*Abies pichta,* or *Abies Sibirica.*
———	———	———	———	———	———	———	———	———
RESIN ACIDS. A. Soluble in Am. carbonate, amorphous, .	Abienic, $C_{13}H_{20}O_2$ (m. p. 114-115°), K_1, cold, 9-10 %.	Pimarinic, $C_{14}H_{22}O_2$, K_1, hot or cold, 6-7 %	—	—	Picea-pimarinic, $C_{13}H_{20}O_2$ (132-135°), 2-3 %, K_1, cold and boiling, I_1.	Canadinic, $C_{19}H_{34}O_2$ (135-136°), 13 %.	Palabieninic, $C_{13}H_{20}O_2$ 5 %. *Sol. in Na_2CO_3.* Palabietinic, (6-7 %), $C_{20}H_{30}O_2$ (cryst.), (153-154° C.) Lævo-rotary.	Beljiabieninic, $C_{13}H_{22}O_2$, 4-5 %. Beljiabietinic, $C_{20}H_{30}O_2$ (cryst.), (2.5-3 %).
B. Insoluble in Am. carbonate.								
a. Crystallisable, ...	Abietolic, $C_{20}H_{28}O_2$ (145-153°), K_1, cold; K_2, hot, 1½-2 %.	Pimaric, $C_{20}H_{30}O_2$ (144-146°), 15-20 %.	Laricinolic, $C_{20}H_{30}O_2$ (147-148°), K_1, more, with excess, 4-5 %.	Silveolic $C_{14}H_{20}O_2$ (138°), K_1, cold and hot, 1½ %, I_1.	Picea-pimaric, $C_{20}H_{30}O_2$ (144-145°), K_1, cold and hot, I_1, 1½-2 %.	Canadolic, $C_{10}H_{28}O_2$ (143-145°), K_1, cold, K_2, (nearly) hot, 3 %.		
b. Amorphous, ...	Abietinolic, $C_{16}H_{24}O_2$, 46-50 %.	Pimarolic, $C_{18}H_{26}O_2$, 48-50 %.	Larinolic, $C_{18}H_{26}O_2$, 55-60 %.	Silvinolic, $C_{15}H_{26}O_2$, 58-60 %.	Picea-pimarolic, $C_{25}H_{44}O_2$, 48-50 %.	Canadinolic, $C_{19}H_{30}O_2$, 48-50 %.	Palabietinolic, $C_{16}H_{24}O_2$, 53-57 %. (α & β).	Beljiabietinolic, $C_{16}H_{24}O_2$, 42-50 %. (α & β).
α-acid, pptd. by alcoholic lead acetate, ...	(95-96°) K_1, cold; more with excess.	(90-91°) K_1, cold or hot.	(80-81°) K_1; more with excess.	(85-90°) K_1, I_1.	(90-95°) K_1; cold and hot I_1.	(89-95°).		
β-acid, not ppted. by alcoholic lead acetate, ...	(93-94°) K_1, cold gradually increasing.		(85-86°) K_1, cold, more with excess of KHO.	(89-95°) K_1, I_1.	(88-94°) K_1, cold and hot I_1.	(90-95°) K_1.		

COMPOSITION OF CONIFEROUS RESINS (CONTINUED).

	STRASSBURG.	BORDEAUX.	VENICE.	FINLAND.	JURA.	CANADA.	TURPENTINE from:—	WHITE PITCH. (Russian "Beljivar.")
INDIFFERENT RESINS. Insoluble in alkalies, . . .	Abietoresene, $C_{19}H_{30}O$ (168–169°), 12–16 %.	Bordoresene, viscid, 5 %.	Resene, indefinite, 14–15 %.	Silvoresene (58–60°), 20–21 %.	Juroresene, $C_{21}H_{36}O$, 10–12 %.	Canadoresene, $C_{21}H_{40}O$ (170°), 1–12 %.	Paloresene, 10 %.	Beljoresene, $C_{31}H_{58}O$, 15–18 %.
ESSENTIAL OIL. A. Readily volatile with steam, ...	b. pt. 162–163°, 24–25 %.	b. pt. 150–175°, 14 %.	b. pt. 157°, 15–16 %.	b. pt. 155–163°, Sp. gr. .840, 15 %.	32–33 %.	23–24 %. Lævo-rotary.	b. pt. 155–172°. 20–22 %. Sp.gr. 0.864. Dextrorotatory.	b. pt. 158–165°C. dextrorotatory, 20 to 30 %. Sp. gr. 0.863. Sol. in 90 % alcohol, 1 : 10.
B. Tailings, ...	4–6 %.	15 %.	b.pt. 190°, 5–6%.	—			—	Traces.
MINOR CONSTITUENTS. *Bitter principle*, *alkaloid*, succinic acid, colouring matter, water, and impurities, .	1–2 %.	2–4 %.	1–2 %.	1–2 %.	1–2 %.	1–2 %.		
REFERENCE. Original, ...	*Arch. Pharm.*, 1900, p. 411.	*Arch. Pharm.*, 1900, p. 630.	*Arch. Pharm.*, 1900, p. 387.	*Arch. Pharm.*, 1901, p. 167.	*Arch. Pharm.*, 1900, p. 616.	*Arch. Pharm.*, 1900, p. 489.	*Arch. Pharm.*, 1902, p. 568.	*Arch. Pharm.*, 1902, p. 584.
Abst. *Jour. Chem. Soc.*	1900, i, 679.	1901, i, 220.	1900, i, 680.	1901, i, 397.	1901, i, 91.	1900, i, 678.	1903, i, 105.	1903, i, 106.

[1] The oleo-resin of *Picea vulgaris* grown at Siebenbürgen gave very similar results to the Jura specimen, but the formula of picea-pimarinic acid is given as $C_{12}H_{20}O_2$, that of the picea-pimarolic acids as $C_{18}H_{28}O_2$, and that of the resene as $C_{19}H_{30}O$ (*Arch. Pharm.*, 1902, p. 272; abst. *J. C. S.*, 1902, i, 551).

common turpentine.[1] Venetian turpentine is sometimes added. For the detection of common rosin, E. Dieterich recommends the Storch-Morawski reaction (page 177). The acid-number of Canada balsam ranges from 80 to 87, and the ester-number from 4 to 10.

According to A. Tschirch, with the exception of amber, all coniferous oleo-resins are free from esters, consisting solely of resin-acids, resenes, and essential oil. These constituents may be separated as indicated on page 142. Only a few of the coniferous resin-acids dissolve in ammonium carbonate solution. The majority are amorphous, are dissolved by sodium carbonate (1 per cent. solution), and may be separated by crystallisation or precipitation with lead acetate.

The resin-acids of copaiba and Zanzibar copal, which are obtained from leguminous plants, present a close resemblance to the coniferous resin-acids.

Tschirch and his collaborators have described a large number of acids and resenes obtained from coniferous resins, but the formulæ and even the existence of many of the substances described require confirmation. The table on page 200 gives a résumé of their results.

Balsam of Copaiba. Copaiva. Capivi.

Copaiba is an oleo-resin obtained from the trunk of *Copaifera Lansdorfii*, and other South American species of *Copaifera*.[2] The proportions of resin and volatile oil in copaiba are very variable, and hence the viscosity and specific gravity are far from constant. The medicinal value of the two constituents of the oleo-resin requires further investigation.

The chemistry of copaiba balsam has been recently investigated by A. Tschirch and by E. Keto (*Archiv der Pharm., ccxxxix, 548; abst. J. S. C. I., 1901, p. 1238*).

There are several well-defined commercial varieties of copaiba balsam which take their names from the port of exportation.

MARACAIBO BALSAM is the only variety of copaiba recognised

[1] A product known in commerce as "Oregon balsam" and consisting of a mixture of colophony and oil of turpentine much resembling Canada balsam, is used as an adulterant of the latter substance. (E. Dowzard, *Chem. and Druggist*, 1904, p. 439). The true so-called Oregon balsam is derived from *Pseudotsuga mucronata*, and its essential oil contains much lævo-pinene. Factitious Oregon balsam of the above composition contains the same proportion of resin as does Canada balsam, and their physical characters are almost identical. The presence of this adulterant is best detected by determining the acid-value of the essential-oil-free resin. Colophony has an average acid value of about 165, while that of the resin of Canada balsam averages 120 to 124.

[2] See Umney and Bennett, *Pharm. Jour.*, 1901, i, 324.

by the German Pharmacopœia. The essential oil distilled from this balsam is typical copaiba oil having a gravity about 0.900 to 0.910, and an optical rotation ranging from —7° to —35°. The residue consists almost entirely of resin-acids, namely: *β-meta-copaivic acid*, $C_{10}H_{16}O_2$, crystallising in pointed prisms melting at 89 to 90°, and *illuric acid*, $C_{20}H_{28}O_3$, melting at 128° C.

PARA BALSAM is very variable in quality, but is remarkable for its fluidity and its high proportion of essential oil. The resin of this balsam contains, besides indifferent *resenes*, *para-copaivic acid*, $C_{20}H_{32}O_3$, crystallising in pointed and quadratic leaflets melting at 145 to 148°, and soluble in ammonium carbonate solution; and *homo-para-copaivic acid*, $C_{18}H_{28}O_3$, melting at 111°, and insoluble in ammonium carbonate, but soluble in sodium carbonate solution.

MATURIN BALSAM is of golden-yellow colour, fairly thick, and is not fluorescent. It has a somewhat more pleasant odour than most varieties of copaiba balsam.

MARANHAM BALSAM is a thick, golden-brown liquid, and is most esteemed for the manufacture of capsules.

AFRICAN (Illurin) BALSAM is of uncertain botanical origin, though probably derived from a species of *Copaifera*. It is distinguished from other copaibas by yielding a dextro-rotatory oil, and its presence in the balsam used in medicine is specially guarded against in the British Pharmacopœia by means of this property. African Balsam has a high specific gravity (0.985 to 1.000), is of fairly thick consistence, exhibits a slight fluorescence, and has a pungent, pepper-like odour. It deposits crystals on standing, and yields about 40 per cent. of volatile oil on distillation with steam (see page 206). The acid-value of Illurin balsam is given as 57 to 60, and the ester-number at from 9 to 10. *Illuric acid*, $C_{20}H_{28}O_3$, the chief resin acid of African balsam, forms hexagonal tables melting at 128° (Tschirch, *Pharm. Central.* 1891, 337). It is probably identical with the crystalline acid described by Umney and by Peinemann, and possibly also with Fehling's "*oxy-copaibic acid.*" The essential oil of African copaiba has, according to Parry and Bennett, been extensively used for the adulteration of peppermint oil.

The characters ascribed to copaiba by different authorities vary greatly. In the British Pharmacopœia of 1885 the gravity was given as ranging from 0.940 to 0.993, but in the edition of 1898 this was extended from 0.916 to 0.995. The U. S. Pharmacopœia (8th Rev.) allows a gravity from 0.950 to 0.995 at 25° C. The German Pharmacopœia, Edition iii, allowed a range from 0.960 to 0.990, but in Edition iv this was restricted to 0.980 to 0.990. These varying requirements are due to the different values attached to the essential oil of copaiba, the B. P. requiring a

minimum of 40 per cent., whereas the G. P. limits the proportion of oil to less than this amount.

The following characters have been recorded by Umney and Bennett (*Pharm. Jour.*, 1901, i, 324) for five specially-selected typical samples of copaiba balsam:—

	BAHIA.	CARTAGENA.	MARACAIBO.	MARANHAM.	PARA.
BALSAM:—					
Specific gravity,	0.938	0.970	0.969	0.990	0.920
Percentage of oil,	49.7	41.3	42.5	41.8	62.4
U.S.P. Ammonia test,	turbid	clear	clear	clear	turbid
Acid-number,	33.7	56.0	50.2	81.5	33.1
Ester-number,	15.3	28.0	12.1	12.8	26.9
RESIN:—					
Physical characters,	*soft*	*brittle*	*firm*	*brittle*	*very soft*
Acid-number,	73.1	135.7	80.3	136.3	68.9
Ester-number,	73.0	45.1	49.9	36.7	87.2

The characters of the essential oil from these samples were not distinctive. The gravity ranged from 0.903 to 0.908, and the boiling point from 245° to 275° C. The oils were soluble in an equal quantity of absolute alcohol, and their optical rotation for 1 decimetre varied from —7° to —21°. The erroneous statement made in the British Pharmacopœia (1898) that the optical rotation of copaiba oil varies from —28° to —34°, is the result of a careless blunder (see F. W. Short, *Pharm. Jour.*, 1900, i, 54). Gildemeister and Hoffmann give the range as from —7° to —35°.

Umney and Bennett (Pharm. Jour., 1901, i, 324) suggest that the official requirements for copaiba balsam should be revised as follows: A more or less viscid liquid, generally transparent and occasionally fluorescent; yellow or brown, having a peculiar aromatic odour, and a persistent acrid, somewhat bitter taste. Specific gravity, 0.975 to 0.995. Entirely soluble in absolute alcohol, and in four measures of petroleum-spirit, the latter solution yielding only a slight filmy deposit on standing. It should evolve no odour of turpentine oil when heated, and should not lose more than 45 per cent. when heated in a water-bath for forty-eight hours. Three measures should form a transparent mixture when added to one measure of ammonium hydroxide (10 per cent.). The volatile oil should have a rotation of —7° to —21° for 100 mm., and should not boil under 250° (absence of African balsam). It should give a negative reaction with the glacial acetic and nitric acids test (p. 208, absence of gurjun balsam[1]). A solution of 1 gramme in 50 cc. of absolute alcohol should neutralise at least 13.5 cc. of decinormal caustic

[1] The presence of gurjun balsam is best detected by the examination of the essential oil, since the colour reactions on the oil are far more sensitive than with the balsam itself.

alkali, on titration with phenolphthaleïn (presence of a sufficient proportion of resin-acids).

The *U. S. Pharmacopœia* (8th Rev.) allows 50 per cent. of oil in balsam of copaiba. It is further directed that one gramme of copaiba, dissolved in 50 cc. of alcohol, should require not less than 2.3 cc., and not more than 2.8 cc. of semi-normal alcoholic potash for neutralisation to phenolphthaleïn. The nitric and acetic acids colour-test for gurjun balsam is included (using, however, 1 cc. of glacial acetic acid). Five cc. of the balsam, when shaken with 15 cc. of alcohol and heated to boiling for one minute, should yield no oily drops to the solution on allowing it to cool and stand for one hour (absence of paraffin oils). Twenty drops of copaiba, when boiled with 1 cc. of alcoholic potash (10 per cent.) solution for two minutes and cooled, and twice the volume of ether added, should not cause the production of a gelatinous mass (absence of fixed oils). One gramme of copaiba, if shaken with 10 ccs. of ammonia-water (10 per cent.), and allowed to stand 24 hours in a closed vessel, will produce a turbid solution, but this should not gelatinise nor should a firm mass be produced (limit of resin).

The *specific gravity* of copaiba balsam varies considerably and only gives reliable indication of the quality of the article when considered in conjunction with the proportion and characters of the volatile oil present. The thinner varieties of balsam containing a high proportion of oil have a specific gravity as low as 0.916 (as in the case of Para balsam), whereas the gravity of the thicker varieties often exceeds 0.990, and occasionally reaches 1.000 or even more. The B. P. limits are from 0.916 to 0.995, but these figures are sometimes slightly exceeded.

As a rule, the colour of copaiba balsam is too deep to allow of the observation of its *optical rotation,* but the optical activity of the essential oil is an important character.

The proportion of *essential oil* in copaiba balsam is very variable. In cases where the balsam is intended for distillation the amount of oil is important. The percentage of oil in genuine balsams usually ranges between 40 and 75 per cent., rarely much exceeding the latter figure. As a rule, the percentage seldom exceeds 60, except in the case of the low gravity Para copaiba. As much as 92 per cent. of oil has been recorded, but such a sample was probably adulterated with turpentine.

Copaiba Resin is not now official in the U. S. Pharmacopœia, (8th Rev.). According to Umney and Bennett, it is soluble in alcohol, ether, and carbon disulphide, forming acid solutions. One gramme should neutralise at least 21.5 cc. of decinormal alkali when titrated in alcoholic solution with phenolphthaleïn.

OIL OF COPAIBA.

The determination of the essential oil present in copaiba is best ascertained from the loss of weight suffered by the sample at about 120° C., when, except in rare cases, the residual resin will be hard and friable. The resin should never exceed 60 per cent., and is frequently as low as 35 per cent. or even less. For the examination of the characters of the oil, 100 grammes of the balsam should be steam-distilled in the usual way. Generally speaking, the only adulterants which will affect the characters of the oil thus obtained are gurjun balsam and turpentine (unless the admixture of African balsam of Copaiba be included[1]). The specific gravity of the oil from genuine copaiba ranges, according to Schimmel & Co., between 0.900 and 0.910, but these limits are too narrow, as pure samples will often yield an oil of sp. gr. 0.898. The limits 0.895 and 0.910 are safer. The optical rotation of oil of copaiba varies between —7° and —35°. (The British Pharmacopœia, however, only allows a range of from —28° to —34°, see page 204.) The oil boils at 250° to 275°.

The oil distilled from pure balsam of copaiba is completely soluble in absolute alcohol and in four times its volume of petroleum-spirit.

The following figures by J. C. Umney show the properties of the oil from African balsam as compared with those of the oils yielded by Maracaibo and Para balsams:—

	AFRICAN.	MARACAIBO.	PARA.
Percentage of Volatile Oil in balsam,	32	42	64.3 to 80.2
Sp. Gravity of Oil at 15° C.,	0.9180	0.9050	0.9060
Rotation in 200 mm. tube,	+20.7°	—34.3°	—28.9°
Solubility in absolute alcohol at 15° C.,	not sol. in 50	1 in 1	1 in 1
Range of boiling point, °C.,	260° to 273°	245° to 255°	252° to 260°

No other differences of importance were observed by Umney, except that the oil from the African balsam reduced auric chloride in chloroformic solution (with 1 per cent. of alcohol), whilst the other oils did not.

Copaiba resin consisting chiefly of free resin-acids, the balsam has a very high acid-number, but an insignificant ester-number. The following table gives the limits for the analytical results

[1] In the presence of African copaiba, the oil obtained by steam-distillation will exhibit comparatively feeble lævo-rotation, or if the proportion be very large, the oil may be dextro-rotatory.

recorded by various observers for the different varieties of balsam of Copaiba:—

Variety of Balsam.	Characters of Balsam.			Essential Oil.	
	Specific Gravity.	Acid-number.	Ester-number.	Per-centage.	Specific Gravity.
Angostura,	0.980 to 1.009	75 to 85	7 to 20	40 to 45	0.906
Bahia,	0.980	34 to 98	5 to 15	40 to 45	0.908
Carthagena,	0.950 to 0.965	56 to 88	5 to 28	50 to 55	0.904
Maracaibo,	0.980 to 0.998	50 to 98	0 to 15	50 to 65	0.895 to 0.907
Maranham,	0.990	81.5	13	42 to 50	0.902
Maturin,	0.980 to 0.988	75 to 85	4 to 13	45 to 50	0.898
Para,	0.915 to 0.990	25 to 62	2 to 33	40 to 90	0.898 to 0.904
Surinam,	0.907 to 0.961	15 to 59	10 to 18	41 to 72	0.910
African (Illurin)	0.985 to 1.00	57 to 60	9 to 10	40	0.918
Gurjun Balsam,	0.955 to 0.980	5.8 to 20	1 to 10	55 to 82	0.915 to 0.930

The wide variations recorded above are probably due to certain of the samples being adulterated.

L. F. Kebler (*Amer. Jour. Pharm.*, 1897, page 577) has published the results of the examination of various samples of commercial copaiba,[1] as have also E. W. Bell (*Pharm. Jour.*, 1900, ii, 99) and E. W. Mann (*Pharm. Jour.*, 1903, i, 419). The last-named found that the greater number of the commercial samples examined by him responded to the colour-tests for gurjun oil, although in other respects they conformed to the description of a genuine sample.

Adulterations of Copaiba Balsam.

Balsam of copaiba is liable to sophistication in various ways, though gurjun balsam, oil of turpentine, castor oil, and colophony are the most usual additions. According to Hager, sassafras oil has been employed, but the price of this oil would usually prohibit this addition.[2]

Gurjun balsam is the product of several species of *Dipterocarpus,* and presents a close general resemblance to copaiba.

[1] Kebler finds that the great majority of commercial samples of copaiba do not respond to the magnesia solidification test, and that no sample having a specific gravity below 0.980 will solidify well. It is therefore only such samples as are very rich in resin and very poor in essential oil that will conform to the test, not now included in the U. S. Pharm. (8th Rev.).

[2] Hager detects oil of sassafras by mixing 1 cc. of the sample with 2 cc. of concentrated sulphuric acid; after the mixture has cooled, 20 cc. of alcohol are added, the mixture heated to boiling, and set aside. With *pure copaiba* a milky greyish or reddish yellow liquid is obtained on addition of the alcohol, and on boiling the liquid becomes clear and yellow, and a resinous compound settles to the bottom. If oil of sassafras be present, addition of alcohol produces a dark brown colour, becoming on boiling still darker with a violet tint.

It is said to contain a crystalline body known as *gurjunol*,[1] $C_{20}H_{28}(OH)_2$, which melts at 126° to 129° C., while, according to Tschirch and Weil, a neutral resene, containing $C_{17}H_{28}O_2$, is present. The specific gravity of gurjun balsam averages about 0.964, while that of the essential oil (which is sometimes present to the extent of 80 to 82 per cent.) ranges from 0.915 to 0.930, and hence in its presence the density of copaiba oil will be slightly raised. Gurjun oil is usually strongly lævo-rotatory (—55° to —130°), but several specimens of dextro-rotatory oil have been met with. As a rule, however, the lævo-rotation of copaiba oil will be considerably increased by an admixture of gurjun oil. Gurjun oil distils almost completely between 255° and 265° C., the main constituent being a sesquiterpene boiling at 255° to 256°, at which temperature a large fraction of the oil passes over.

The recognition of gurjun balsam in copaiba has been studied by L. F. Kebler (*Amer. Jour. Pharm.*, lxvii, 394), who considers that no dependence can be placed on the physical characters of a sample. He regards the ammonia test as misleading, the acid-number as unreliable, and Hager's colour-test[2] as unsatisfactory, especially if the proportion of gurjun balsam be less than 25 per cent. Kebler recommends the following modification of a test described by Dodge and Olcott, which is capable of detecting as little as 5 per cent. of gurjun oil in copaiba. Four drops ofthe balsam are added carefully to a mixture of 10 cc. of glacial acetic acid (99.5 per cent.) with four drops of nitric acid (1.42 sp. gr.). In a few minutes a reddish zone will form between the layer of balsam and the acid mixture if gurjun balsam be present, and on mixing the contents of the tube the whole will assume a reddish or purple colour, varying in intensity with the proportion of gurjun balsam. This test is best applied to the essential oil distilled from the sample. A reaction which Kebler regards as fairly reliable when a moderately large proportion of gurjun balsam is present is the transient red or violet tinge produced on dissolving one drop of the suspected balsam in 20 drops of carbon disulphide, and adding one drop of a cooled mixture of equal volumes of strong sulphuric and nitric acids (Flückiger).

These colour-tests may with advantage be also applied to the distilled oil, since certain fish-liver oils give evanescent violet

[1] Gurjunol is converted into the acetate, $C_{20}H_{28}(C_2H_3O_2)_2$, when boiled with sodium acetate and acetic anhydride. This compound crystallises in small needles melting at 74° to 75° C.

[2] Hager adds 6 drops of the balsam to 3 cc. of a solution of 1 part of strong sulphuric acid in 25 of acetic ether, when a violet colour, changing slowly to brown and black, is produced in presence of gurjun balsam.

colours, and these oils are not, of course, found in the distillate. Oil of valerian is also said to give a similar coloration.

Copaiba balsam adulterated with gurjun balsam is not quite clear, and frequently exhibits prisms of gurjunic acid under the microscope. According to E. Hirschsohn, gurjun balsam is incompletely soluble in ether, whereas copaiba balsam gives a clear solution. Alcoholic lead acetate solution gives a cloudiness with an alcoholic solution of copaiba, which disappears on warming, while with gurjun balsam no reaction takes place.

For the determination of *fatty oils*, J. Muter (*Analyst*, i, page 160) recommends a process based on the insolubility of oleate and ricinoleate of sodium in ether-alcohol, and the solubility of the sodium salts of copaiba resin-acids in the same solvent.

For the detection of *castor oil* in copaiba balsam L. Maupy (*Jour. Pharm. Chim.*, 1894, page 362; abst. *J. S. C. I.*, 1894, page 981) recommends the following method, based on the fact that castor oil yields *sebacic acid* and *caprylic alcohol* on dry distillation with excess of caustic alkali: Ten grammes of the sample is heated with dry caustic potash in a silver dish. The mass is stirred and heated until all the volatile oily matters are driven off. In the presence of castor oil, the odour of caprylic alcohol will be noticeable. On cooling and thoroughly separating the upper resinous layer, the lower white liquid portion is treated with 50 cc. of water, boiled and filtered. Sebacic acid separates out on cooling if the sample contained castor oil. The acid may be further identified by converting it into the lead salt.

The presence of fatty oils in copaiba balsam renders the separated resin soft, and reduces the percentage of essential oil in the sample. The specific gravity and acid-number of the sample are also lowered, while the ester-number is raised.

According to Hager (*Year-Book Pharm.*, 1871, p. 64), Venice turpentine is occasionally employed as an adulterant of copaiba.

Oil of Turpentine may be readily detected in copaiba balsam by steam-distilling the sample, the volatile oil of the balsam and the oil of tnrpentine passing over. The latter distils before the copaiba oil, oil of turpentine boiling at about 160°, and oil of copaiba at 240° to 250° C. The odour of the turpentine can be detected when the first few drops of distillate are heated on a watch-glass, by which means 2 or 3 per cent. of the adulterant may be detected. An idea of the amount of oil of turpentine present may be obtained by observing the density and boiling-point of the distilled oil. The presence of oil of turpentine in copaiba balsam reduces the specific gravity, and lowers the acid and ester numbers, while it increases the percentage of essential oil, which has a lower specific gravity and optical rotation than genuine oil of copaiba.

Cativo, from *Prioria copaifera*, presents no similarity to copaiba balsam, although it has been supposed to resemble it. (See E. M. Holmes; J. C. Umney; *Pharm. Jour.*, 1902, ii, 296.)

GUM-RESINS.

The gum-resins constitute a group of natural products which occur as exudations from various plants. These products consist of a mixture of gums with various resins, a small percentage of essential oil, and traces of colouring and undefined matters.

The gum-resins occur in commerce either in tears or masses. The tears are the purer form, as they usually consist of the pure exudatiou, whereas the latter variety is liable to accidental admixtures, such as woody fibre, &c., besides intentional adulterations of a varied kind. Stones, sand, gypsum, &c., are among the mineral sophistications practised, and adulteration with colophony and other low-priced resinous matters is also met with.

When the natural gum-resins are treated with water, gum, sugar and other carbohydrates are dissolved, but the extraction is apt to be imperfect owing to the protective action exerted by the resinous constituents. A better method of proximate analysis is to treat the substance with alcohol of 95 per cent. strength, which dissolves the resinous matters, leaving the carbohydrates practically intact, and these can then be readily extracted with water, any woody fibre or added mineral matters being left as a residue.

Mauch's method (page 148) is well suited for the resolution of gum-resins.

Ammoniacum.

This gum-resin is the product of *Dorema ammoniacum*, one of the *Umbelliferæ*.[1] It occurs in commerce in tears, and in masses of agglutinated tears, which are apt to contain extraneous matters. At ordinary temperatures ammoniacum is hard and brittle, but softens by the heat of the hand. It has a faint, somewhat unpleasant odour, which is accentuated on warming.

A specimen of ammoniacum examined by Tschirch, Luz and Osterle contained 3.5 per cent. of matter insoluble in alcohol, and water, in addition to the salicylic ester of *ammoresinotannol*, $C_{18}H_{29}O_2.OH$; traces of free salicylic acid; volatile acids such as

[1] The so-called *African ammoniacum* is obtained from *Ferula tingitana*, and differs from the ordinary or Persian product in containing *umbelliferone* (compare Galbanum, page 215).

acetic and caproic acids; and about 0.5 per cent. of essential oil. No sulphur or umbelliferone could be detected.

The following analyses of apparently authentic samples of ammoniacum have been recorded:—

Number.	Ethereal Oil. (*Per cent.*).	Water. (*Per cent.*)	Ash. (*Per cent.*).	Gum. (*Per cent.*).	Resin. (*Per cent.*).	Observer.
1, ...	1.27	5.10	2.00	26.10	65.53	Plugge.
2, ...	...	...	...	22.4	72.0	Buchholz.
3, ...	...	...	...	18.4	68.6	Braconnot.
4, ...	...	...	...	19.3	...	Moss.
5, ...	1.43 to 6.68	0.81 to 3.27	2.02 to 3.27	...	47.2 to 69.2	Hirschsohn.

According to some authorities, a small quantity of gelatinous matter and sugar are also present.

The following analytical limits and characters of varieties of ammoniacum have been recorded:—

	A. Kremel.		E. Dieterich.		Beckurts & Brüche.	
	Persian.	African.	Crude Persian.	Purified Persian.	Purified Persian.	Persian in tears.
Specific gravity, ...	...	...	...	...	1.19 to 1.21	1.20
Ash, per cent., ...	...	...	...	...	0.79 to 4.47	3.84
Resin soluble in 96 per cent. alcohol, .	...	...	46 to 88	66 to 76	59 to 68	56
Acid-number (of resin), ...	100 to 112	59	57 to 105	79 to 135	69 to 80	70
Ester-number (of resin), ...	30.6 to 50.5	123	64 to 91	73 to 98	19 to 38	35

By dissolving ammoniacum in a 60 per cent. aqueous solution of chloral hydrate and pouring the solution into strong alcohol, Mauch obtained 21 per cent. of pure gum.

According to Gregor and Bamberger, the methoxyl-number of ammoniacum ranges from 8.6 to 11.0.

Asafœtida.

This gum-resin is the product of several species of *Ferula*, probably chiefly of *F. scorodosma*, *F. Narthex*, and, according to the British Pharmacopœia, *F. fœtida*. Asafœtida is largely imported from Bombay, to which place it is brought by the gatherers from Persia.

Asafœtida is extensively used in America in the treatment of a disease of horses known as "heaves." The gum-resin is

also employed in small quantity as a flavoring agent, in sauces, &c.

The British Pharmacopœia of 1885 described asafœtida as occurring "rarely in tears; usually in irregular masses," but in face of this fact the edition of 1898 describes asafœtida as occurring "in rounded or flattened tears." Tears of asafœtida are so scarce that were the consumers (chiefly veterinary surgeons) restricted to this form, the supply would be insufficient. The tears are much purer than asafœtida in masses, which is contaminated with much dirt and woody fibre.

According to Tschirch, the chief constituent of asafœtida is the *ferulic ester* of the alcohol *asaresinotannol*, $C_{24}H_{34}O_5$. This ester forms about 60 per cent. of the resin, besides which there are present traces of the free alcohol and free ferulic acid; 25 per cent. of gum; traces of vanillin; and up to 7 per cent. of an essential oil of complex nature.

Commercial asafœtida is sometimes adulterated with cheaper resins, such as colophony, but the most common impurity is an abnormal proportion of mineral matter. The British and United States Pharmacopœias require that asafœtida should not yield more than 10 per cent. of ash, while the German Pharmacopœia fixes 6 per cent., and the Dutch Pharmacopœia 20 per cent. as the ash-limit. Mörner and Fristedt examined a sample of asafœtida in tears, which contained 86 per cent. of mineral matter, consisting chiefly of calcium sulphate. J. Muter has also described samples of asafœtida containing as much as 70 per cent. of stones. These no doubt had their origin in the practice, formerly much in vogue in the East, of packing drugs with as many heavy fragments of stone as could be got into the bale or cask.

W. A. Buckner (*Year-Book Pharm.*, 1891, page 211) found five samples of asafœtida to contain from 27 to 45 per cent. of their weight of matters soluble in 90 per cent. alcohol, while one other sample contained 59.5 per cent. of alcohol-soluble matter. The ash of the five samples ranged from 19.45 to 56.03 per cent., the portion insoluble in hydrochloric acid varying from 1.37 to 21.96 per cent.

From an examination of eleven samples of asafœtida, Martin and Moor (*Analyst* (1900), xxv, 2) found the ash to range from 26.4 to 63.1 per cent., and the ash insoluble in hydrochloric acid to range from 42 to 84 per cent. of the total, while in one case the ash dissolved readily in hydrochloric acid with much effervescence, leaving only 3.6 per cent. insoluble. The proportion of the sample soluble in 90 per cent. alcohol ranged from 14.8 to 39.8 per cent. in twelve samples. (Similar figures have also been published by R. W. Moore, *Jour. Soc. Chem. Ind.*, 1899, page 987; M. I. Wilbert, *Amer. Jour. Pharm.*, 1901, page 131; and others.)

The ash yielded by asafœtida does not afford an accurate criterion of the mineral matter of the sample, as the sulphur present exists, to a great extent, in organic combination and is fixed by the bases; while a portion of the sulphate is liable to be reduced during ignition by the organic matter. Hence Mauch treats the sample with ten to fifteen times its weight of 60 per cent. chloral hydrate solution in water,[1] when the gum and resin slowly dissolve. The residue is washed on to an ashless filter-paper with chloral hydrate solution, and then washed with alcohol, and after drying the residue is ignited and weighed.

Since by far the greater proportion of commercial asafœtida contains considerably more than 10 per cent. of mineral matter, in order to obtain specimens of B. P. quality either fine tears must be used, or the purified resin from which the mineral matter has been removed must be employed.[2]

In addition to an ash-limit of 10 per cent., the British Pharmacopœia further requires that asafœtida shall contain not less than 65 per cent. of matter soluble in alcohol of 90 per cent. strength. The United States and German Pharmacopœias require only 50 per cent. of soluble matter under these conditions. It is held by most authorities that the British Pharmacopœia requirements of ash and matter soluble in alcohol are unpractical and far too stringent, and that an ash-limit of 20 per cent., and an alcohol-solubility of not more than 50 per cent., would be preferable.

According to Hirschsohn, good samples of asafœtida should yield not less than 11 per cent. of soluble matter to petroleum-ether when the residue is dried at 17° C., and not less than 6 per cent. of this residue should be lost on being heated to 120° C. The use of these arbitrary temperatures is rendered necessary by the occurrence of volatile soluble constituents in asafœtida. Eleven samples of the gum-resin were found by Hirschsohn to give the following results by treatment with petroleum-ether:—

Extract, dried at 17° C., ... from 1.50 to 13.45 per cent.
Extract, dried at 120° C., ... from 1.01 to 4.65 per cent.

The following table gives the acid- and ester-numbers of asafœtida according to several observers. The figures refer to the

[1] Whether by a "60 per cent. solution" is meant a mixture of 60 parts of chloral hydrate with 40 of water, or a solution of 60 grammes of chloral hydrate in 100 cc. of water is uncertain.

[2] To purify asafœtida H. W. Jones (*Y. B. Pharm.*, 1900, page 503) recommends that a filtered solution of the gum-resin in five parts of 90 per cent. alcohol should be poured into ten times its bulk of cold water faintly acidulated with hydrochloric acid. After standing twenty-four hours, the precipitated asafœtida is collected and allowed to dry in the air.

extracted gum-resin, with the exception of those obtained by K. Dieterich, which lose their meaning unless the ash is known:—

Character of Sample.	Acid-number.	Ester-number.	Observers.
Extracted gum-resins, ...	27 to 55	145 to 182	A. Kremel.
" " ...	11 to 82	82 to 129	E. Dieterich.
" " ...	27 to 43	181 to 214	Beckurts and Brüche.
Commercial samples, ...	*65 to 80*	*80 to 130*	*K. Dieterich.*

According to Gregor and Bamberger, the methoxyl-number of asafœtida ranges from 7 to 18.

Tincture of Asafœtida, B. P., is prepared by extracting 200 grammes of the gum-resin with one litre of 70 per cent. alcohol. The solubility of asafœtida in alcohol of this strength is sometimes more and sometimes less than its solubility in 90 per cent. alcohol, and since the gum-resin, as usually met with, rarely comes up to the pharmacopœial standard of alcohol-solubility, the resulting tincture will practically never contain the calculated standard of solid matter in solution. Thus, if 65 per cent. (the pharmacopœial standard) of asafœtida were soluble in 70 per cent. alcohol, the tincture should contain 13.0 grammes of extract per 100 cc. Martin and Moor, however (*Analyst*, xxv, 3), found that the total solids from seven samples of the tincture ranged from 4.3 to 8.5 grammes per 100 cc. Tincture of asafœtida is therefore always much below its presumed strength, and the minimum amount of extract the tincture should contain should be specified. J. C. Umney (*Pharm. Journ.*, 1902, ii, 492) considers 10 grammes of solids per 100 cc. of tincture to be a reasonable standard. The specific gravity of tincture of asafœtida ranges from 0.910 to 0.915.

Oil of Asafœtida is a liquid of disgusting odour, having a specific gravity of about 0.975 to 0.990, and an optical rotation of about $-10°$ in a 100 mm. tube. The oil was examined by Hlasiwetz in 1849, who stated that it was composed of *hexenyl sulphide*, $(C_6H_{11})_2S$, and hexenyl disulphide, $(C_6H_{11})_2S_2$, and was devoid of any oxygen or nitrogen. According to Brannt, asafœtida oil contains allyl sulphide and disulphide. Semmler, however, denies the accuracy of these results, and found the oil to contain pinene; a sesquiterpene having an odour resembling lavender; sulphur compounds having the composition $C_7H_{14}S_2$ (about 45 per cent.), $C_{10}H_{20}S_2$ (the constituent to which the oil owes its odour, about 20 per cent.), $C_8H_{16}S_2$, and $C_{10}H_{18}S_2$; and an oxygenated body having the formula $(C_{10}H_{16}O)_n$, present to the extent of about 20 per cent. This substance, by treatment with sodium, yields cadinene.

Elemi.

The chief Elemi resin of commerce is that from Manila, and is the product of *Canarium commune*. Several of the *Burseraceæ*, however, contribute to the resin as generally known.

When fresh, Elemi is a clear, pale liquid consisting of resins dissolved in essential oil, with a small amount of crystallised resins in suspension. On keeping it changes to a soft crystalline yellow resin, and sometimes becomes quite hard. The odour of fresh Elemi resembles that of lemons or oil of turpentine.

The chemistry of Manila elemi has been investigated by Tschirch and Cremer (*J. C. S.*, 1902, lxxxii, i, 812). The leading constituents appear to be a mixture of two crystalline resins, *a*- and *β-amyrin*, $C_{30}H_{49}OH$; *a*- and *β-elemic acids*, $C_{37}H_{56}O_4$ and $C_{44}H_{80}O_4$; an amorphous *resene*, $C_{15}H_{30}O$; and *bryoidin*, $C_{21}H_{42}O_3$, together with an essential oil consisting of dextro-phellandrene and dipentene. Carana elemi (from *Protium carana*) and Colophonia elemi (Mauritius) have also been investigated by Tschirch and Saal (*Arch. der Pharm.*, ccxli, 149), and Caricari elemi (Brazilian) by Tschirch and Reutter (*Arch. der Pharm.*, 1904, ccxlii, 117). All these varieties contain the two isomeric amyrins.

The analytical characters of Manila elemi are given in the table on page 150.

Galbanum.

This gum-resin is the product of *Peucedanum* (*Ferula*) *galbanifluum* and allied species of the *Umbelliferæ*.

Galbanum when fresh is soft and usually contains about 9 per cent. of essential oil,[1] but the exceptional proportion of 22 per cent. has been recorded. In addition to essential oil, galbanum contains about 27 per cent. of gum and impurities, and about 64 per cent. of alcohol-soluble resin. This contains traces of free *umbelliferone* with about 20 per cent. of umbelliferone present as an ester of *galbaniresinotannol*, $C_{18}H_{29}O_2.OH$, a compound isomeric with the resin-alcohol of ammoniacum. The umbelliferone may be detected by boiling the sample with hydrochloric acid, and adding excess of ammonia to the filtrate, when a beautiful blue fluorescence will be produced.

The following table shows the analytical characters of galbanum as recorded by various observers:—

[1] *Oil of Galbanum* was included in the 1589 edition of the *Dispensatorium Noricum* and in the *Pharmacopœia Augustana* of 1580. It is a yellow oil of specific gravity 0.910 to 0.940, and has an optical rotation of + 20° to —10°. According to Hirschsohn, Persian galbanum yields a dextro-rotatory, and the Levant gum-resin a lævo-rotatory oil. The constituents of the oil include pinene and cadinene.

	A. Kremel.	E. Dieterich.		Beckurts and Brüche.	
		Crude Resin.	Purified.	Crude Resin.	Purified.
Spec. gravity, ...	...	...	...	1.109 to 1.133	...
Ash, per cent......	...	0.4 to 31.3	0.1 to 2.1	4.0 to 8.7	...
Loss at 100° C., per cent........	...	1.1 to 31.0	8.6	...	...
Solubility in 96 per cent. alcohol, = resin, per cent.,..	74.3; 74.2	17.8 to 71.5	45.6 to 92.2	54 to 63	...
On the extracted resin. Acid No...	28.3; 28.3	5.2 to 68.8	19.3 to 46.3	...	19 to 40
On the extracted resin. Ester No...	119.3; 132.2	82.1 to 179.0	55.7 to 91.4	...	63 to 91

Myrrh and Bdellium.

These closely-allied substances are the oleo-resinous exudations from the stem of various species of *Balsamodendron* or *Commiphora*.

At least two distinct varieties of myrrh occur in commerce besides several of bdellium. There is considerable confusion concerning the species of plants which yield true or *Herabol myrrh*, as distinguished from *Bisabol myrrh* and from *bdellium*.[1]

Myrrh formerly came chiefly from Turkey, but now is collected principally in India, Arabia, and Somaliland.

As imported into the United Kingdom, myrrh consists of a mixture of true or Herabol myrrh with several allied products obtained from trees of the same genus (*Commiphora* or *Balsamodendron*). These admixtures are picked out on arrival, so that the "gum myrrh elect" is free from them. The chief gum-resins imported in admixture with Herabol myrrh are opaque bdellium, African and Indian bdelliums, and Bisabol myrrh or opopanax, used for the production of oil of opopanax.

When fresh, myrrh is pale in colour, and soft, owing to the presence of a small percentage of essential oil. When this evaporates, the substance hardens, and darkens in colour to yellow, red, or nearly black.

Herabol Myrrh is the only kind of myrrh officially recognised in pharmacy. It is stated to contain from 50 to 60 per cent. of a *gum* of the formula $C_6H_{10}O_5$; two dibasic *resin acids* containing respectively $C_{13}H_{16}O_8$ and $C_{26}H_{32}O_9$; and *herabol-resene*, $C_{26}H_{34}O_5$, which, according to O. Kohler, contains three hydroxyl groups, though this statement is disputed by Tschirch. Tschirch and Bergmann have given empirical formulæ for vari-

[1] The botany of the species yielding myrrh and bdellium has been exhaustively described by E. M. Holmes, *Pharm. Journ.*, xix, 1898, p. 547; 1899, pp. 26, 77.

ous bodies they claim to have isolated from Herabol myrrh, but the chemistry of the subject is in a very confused state.

Bisabol Myrrh is largely used in China for the manufacture of joss-sticks. In appearance it closely resembles true myrrh, and acquires the taste of the latter when the two are packed together. The taste of Bisabol is, however, very different, and if used in making *Mist. ferri comp.* it gives the preparation a bitter taste. According to Tucholka, Bisabol myrrh contains two *resin acids*, to one of which he assigns the formula $C_9H_{13}O_2$; a neutral *resin* of ketonic character, $C_{20}H_{32}O_4$; and *bisabol-resene*, $C_{29}H_{47}O_8$.

Good samples of myrrh should contain not less than 30 per cent. of alcohol-soluble resin, and should leave not more than 8 per cent. of ash on ignition (many samples give not more than 4 to 5 per cent.). According to K. Dieterich, Herabol myrrh may yield as much as 50 per cent. to alcohol, whereas the proportion of resin in Bisabol myrrh is much smaller (sometimes 20 per cent.). E. Dieterich states the proportion of myrrh soluble in 96 per cent. alcohol at 23 per cent., and the water-soluble constituents at 37 to 52 per cent. These figures probably refer to Bisabol myrrh.

Tucholka found a sample of *Bisabol myrrh* to contain: gum soluble in water, 22.1; gum soluble in soda solution, 29.85; resin, 21.5; bitter principle, 1.5; ethereal oil, 7.8; water, 3.17; and inorganic and insoluble vegetable matters, 13.4 per cent.

According to Flückiger, pure samples of *bdellium* contain about 70 per cent. of resin, 30 of gum, and traces of essential oil. The constituents of bdellium resin are not understood, but are probably closely allied to those of myrrh. African and Indian bdellium are sometimes employed in varnish-making.

Hirschsohn states that myrrh should not contain more than 6 per cent. of matter soluble in petroleum-ether, any larger amount indicating adulteration.[1] He found the following proportions of matter soluble in petroleum-ether in samples of genuine bdellium:—

Origin.	Dried at 17° C.	Dried at 120° C.
India,	13.37	11.29
"	16.57	9.87
Africa,	36.09	35.61
"	35.68	34.79
"	21.70	20.31

[1] This experience is strangely at variance with that of H. G. Greenish, who found a sample of genuine myrrh (previously mixed with twice its weight of sand) to yield 22.8 per cent. to petroleum-spirit (boiling under 80° C.), while the residue yielded 3.96, 3.72, and 2.55 per cent. respectively to carbon disulphide, ether, and alcohol used successively.

For the determination of the gum in myrrh, Mauch dissolves from one to two grammes of the sample in 15 grammes of a 60 per cent. solution of

The presence of sulphur in the residue left after treatment of the sample with petroleum-ether is said by Hirschsohn to indicate the presence of bdellium, but this observation requires confirmation.

The following figures for myrrh and bdellium have been recorded by Kremel. The figures all refer to the resin extracted by alcohol, and not to the original gum-resin.

	Sol. in Alcohol (Per cent.)	Acid-number.	Ester-number.	Sapon.-number.
Myrrh:				
Herabol,	39.5	64.0	95.0	159.0
Herabol,	42.0	60.2	116.5	176.7
Herabol,	23.9	70.3	145.8	216.1
Indian (? Bisabol),	30.7	42.1	130.8	172.9
Bdellium,	74.3	28.3	119.3	147.6

The following results were obtained by K. Dieterich on samples first thoroughly triturated with water, and thus the substance employed contained gummy matters, &c., as well as resin. The ester values were found by difference.

Myrrh.	Acid-number.	Ester-number.	Sapon.-number.	Soluble in Alcohol (Per cent.)
Herabol myrrh,	25.5	204.1	229.6	20
Bisabol myrrh,	20.1	125.5	145.6	50

Gregor and Bamberger found a methoxyl-number of about 13 for genuine myrrh.

On treating true myrrh with nitric acid a violet coloration is produced. On this reaction various tests for myrrh have been based, some of which (including that of the British Pharmacopœia of 1898) afford remarkable examples of badly-devised and unsatisfactory applications. The subject has been investigated by H. G. Greenish (*Pharm. Jour.*, 1901, ii, 666), who finds that the violet colour is yielded in the greatest intensity and purity by adding nitric acid to the ethereal or petroleum-spirit extract of the myrrh.[1]

chloral hydrate in water, and precipitates the filtered liquid by adding 100 grammes of strong alcohol. He obtained 75.2 per cent. of gum by this method.

[1] Greenish found the essential oil obtained by steam-distillation of myrrh to give the reaction with great intensity, but the residue left in the distillation-flask also gave the reaction, though he considered it possible that this might have been due to the incomplete volatilisation of the

The method of applying the test recommended by Greenish is to treat 0.5 gramme of the coarsely-powdered sample of myrrh with 10 cc. of ether, and shake at intervals during ten minutes. Two cc. of the filtered liquid is evaporated at a gentle heat, and the capsule containing the residue inverted over another containing strong nitric acid, so that the residue may be exposed to the acid fumes. When thus treated, the residue from Herabol myrrh gradually acquires a violet colour.

Experiments made by A. R. Tankard, in the author's laboratory, generally confirmed Greenish's observations. The residue obtained on evaporating an alcoholic solution (B. P. tincture) of myrrh gave the violet reaction very imperfectly; but by diluting the tincture with water, and agitating the liquid with petroleum-spirit, the bodies to which the reaction was due passed into the latter,[1] and on separating and evaporating the petroleum-spirit, the residue gave the reaction very distinctly. Tankard prefers to moisten the residue with nitric acid (sp. gr. 1.42) instead of exposing it to the vapour of the acid. Bromine-vapour and bromine-water, which have been recommended, give the coloration much less distinctly. Three samples of Bisabol myrrh examined by Greenish gave no violet coloration with nitric acid, but readily responded to Tucholka's test for Bisabol. Bdellium, hotai, and other allied gum-resins gave Greenish a negative reaction with the nitric acid test.

Old myrrh gives the nitric acid reaction far less distinctly than fresh specimens, probably owing to volatilisation of the essential oil and oxidation of the resinous matters. In any case, the reaction only serves for the recognition of Herabol myrrh in presence of Bisabol, bdellium, &c., and it is of no service for the detection of the latter gum-resins in admixture with true myrrh.

According to Tucholka (*Year-Book Pharm.*, 1898, p. 180), a direct test for Bisabol myrrh consists in treating six drops of the solution of the sample in not less than 15 parts of petroleum-ether with 3 cc. of glacial acetic acid, and then cautiously adding without agitation 3 cc. of strong sulphuric acid. In the presence of Bisabol myrrh a rose-red coloration is produced at the junction of the two strata, and the whole of the acetic acid layer shortly acquires a red colour which persists for some time. When Herabol myrrh is similarly treated only a slight rose coloration is communicated to the acid layer, and this does not increase, while the contact-line is first green, which changes to brown

essential oil, since the fixed residue retained the odour of myrrh (and gave the violet coloration) after being kept for several weeks "on the top of the air-oven."

[1] On distilling the petroleum-spirit solution with steam both the distillate and the resinous residue in the flask gave the nitric acid reaction.

with a greenish fluorescence. The essential oil from Bisabol myrrh gives the rose-red colour-reaction very distinctly.

TINCTURE OF MYRRH, B. P. and U. S. P., is prepared by macerating 200 grammes of coarsely-powdered myrrh with a sufficient quantity of 90 per cent. alcohol, allowing the mixture to stand with frequent agitation for seven days (3 days, U. S. P.), and making the volume finally up to one litre.

The distillation process is not directly available for the determination of the alcohol in tincture of myrrh. A useful method, devised by the author, is described in Vol. I, under "Tinctures."

Thorpe and Holmes (*Proc. Chem. Soc.*, 1903, xix, page 13) have described the following distillation method for the determination of ethyl alcohol in tinctures, essences, &c., containing essential oils and volatile substances such as ether, chloroform, camphor, &c. Twenty-five cc. of the tincture or other liquid, measured at 15.5° C., is diluted with water in a separating-funnel to about 100 or 150 cc., and sufficient common salt added to saturate the liquid. Fifty to 80 cc. of petroleum-ether (boiling below 60°) is now added, and the mixture shaken vigorously for five minutes. After allowing the liquids to stand for half an hour, the lower layer in the separating-funnel is drawn off and extracted a second time with petroleum-ether, if necessary, after which it is placed in a distilling-flask. A single extraction will in most cases be found sufficient. The petroleum-ether extracts are washed successively with 25 cc. of saturated brine, the washings being added to the main quantity of solution in the distilling-flask. The liquid in the flask is neutralised if necessary and is then distilled, the distillate being made up to 100 cc., and its specific gravity determined as usual. The results obtained require a small correction, owing to the fact that the alcohol present in the tincture is diluted in the distillate to four times its original volume, and the errors of the alcohol tables are thus increased. The mean error of the tables at below 40 per cent. proof (for example, 0.972 spec. gravity) may be taken as + 0.2 per cent. of proof spirit, and hence the percentage of proof spirit found by the above method requires a correction of 0.8 per cent., which amount should be subtracted from the result obtained. The method is said to be accurate and to admit of very general application.

J. F. Liverseege (*Chem. and Druggist*, April 18, 1896) has described an indirect method for the determination of the alcoholic strength of tincture of myrrh, which he considers preferable to any distillation process.

Great variations in the amount of solids of tincture of myrrh have been observed (T. Macfarlane, *Canadian Bulletin*, No. 34), which are due to the variable amount of alcohol-soluble matters present in the gum-resin. Myrrh containing 30 per cent. of

alcohol-soluble matter, of which only about 5 per cent. is volatile at 100° C., should yield a tincture containing about 5.5 grammes of solids per 100 cc. (C. G. Moor, "*Suggested Standards for Foods and Drugs*," page 193).

From the examination of a large number of commercial samples of tincture of myrrh by various observers, the specific gravity at 15.5° was found to range from 0.848 to 0.856, the grammes of solids per 100 cc. from 3.0 to 6.1, and the alcoholic strength from 82.7 to 86.8 per cent. by weight.

OIL OF MYRRH was obtained by Tucholka from Somaliland Bisabol myrrh by shaking out the alcoholic resin solution with petroleum-spirit, evaporating the solvent, and steam-distilling the residue. As thus obtained, oil of myrrh is a pale yellow limpid oil of characteristic odour, having a specific gravity of 0.8836 at 24°, and boiling at 220° to 270° C. It has an optical rotation of —14.3° in a 100 mm. tube, and is alleged to contain a new terpene, *bisabolene*.

VOLATILE OR ESSENTIAL OILS.[1]

The great majority of the products known as *essential oils*[2] are proximate principles occurring in nature ready-formed, or as glucosides which by the action of water or enzymes readily undergo decomposition into essential oils and one or more other bodies. The characteristic odours of plants are due, in many cases, to the presence of essential oils.

Broadly speaking, the essential oils differ from the fixed or fatty oils by being volatile without leaving more than an insignificant residue.[3] Hence they do not produce a permanent, translucent, oily mark on paper. In most cases, also, the essential oils possess strong and characteristic odours.

EXTRACTION OF ESSENTIAL OILS.

The volatile oils of plants are obtained:—

(*a*) By *pressure,* as the oils of laurel, lemon, and bergamot.

(*b*) By *distillation with water*, or by passing a current of *steam* through the matter to be extracted. This is the most common and generally applicable method.

(*c*) By *fermentation and distillation;* as, for instance, with the essential oils of mustard and bitter-almonds, the seeds containing no ready-formed oil, but the latter being produced when the crushed seeds are left in contact with water, owing to the influence of peculiar nitrogenised ferments, the oil formed being then separated by distillation with water.

(*d*) By *solution in a fixed oil* devoid of odour, such as olive oil or lard (the "enfleurage" process). The scents of various plants are extracted in this manner.

Many of the oxygenated and sulphuretted constituents of essential oils have been prepared synthetically.

[1] The author is indebted to Mr. E. J. Parry for perusal and criticism of this Section.

[2] French: *Huiles Essentielles, Essences.* German: *Flüchtige Oele.*

[3] In a few instances the natural essential oils contain a notable proportion of non-volatile matter. Bergamot oil leaves from 5 to 6 per cent. of non-volatile residue (Parry).

Composition of Essential Oils.

Essential oils are usually of very complex composition, and different specimens from the same botanical source often exhibit considerable variations in the proportions of their constituents. The essential oils may be arranged broadly in the following seven classes:—

a. Oils consisting chiefly of *terpenes*, $C_{10}H_{16}$, and oxidised products allied thereto; *e. g.*, oil of turpentine, oil of lemon.

b. Oils consisting chiefly of *sesquiterpenes* (cedrenes), $C_{15}H_{24}$, and oxidised products allied thereto; *e. g.*, oil of cedar, oil of cubebs.

c. Oils consisting chiefly of *open-chain terpene-alcohols* and the corresponding *aldehydes; e. g.*, oil of rose, oil of citronella.

d. Oils consisting chiefly of *phenoloid bodies; e. g.*, oil of thyme, oil of cloves.

e. Oils consisting chiefly of *aromatic aldehydes, ketones*, or allied bodies; *e. g.*, oil of bitter almonds, oil of cinnamon, oil of caraway.

f. Oils consisting chiefly of *esters; e. g.*, oil of wintergreen.

g. Oils consisting chiefly of *sulphuretted compounds; e. g.*, oil of mustard, oil of garlic.

General Characters of Essential Oils.

The essential oils of plants are usually liquid at ordinary temperatures, but many of them deposit solid bodies called *stearoptenes* by sufficient cooling. The essential oils have marked, and in many cases characteristic, odours. They volatilise rapidly at ordinary temperatures, though their boiling-points are mostly somewhat high. Essential oils are usually colourless or yellow when freshly prepared, but a few have a well-marked blue colour (see page 249). Some oils rapidly darken on exposure to air and light. Oils which contain aromatic aldehydes often deposit crystals of the corresponding acids on exposure to air.

Those volatile oils which consist chiefly of terpenes are very prone to change in contact with air and moisture, especially in presence of light. The chief products of such change are ill-defined resinous bodies, the chemistry of which is but little understood. There is no evidence of the conversion of the hydrocarbons into any of the normal odorous constituents of such oils. On the contrary, Charabot has deduced evidence that, in some cases, the terpenes result from the dehydration of pre-formed alcohols, during the development of the plant.[1]

[1] Charabot considers that the formation of the chief constituents takes place in two stages, the first of which determines the elaboration of alcohols, which by the elimination of water or by esterification are con-

Most of the essential oils are optically active. In a number of cases the rotatory-power only varies between well-defined limits, so that this function is of great value in the examination of the oils. In the case of certain other oils liable to alteration by age and exposure, the optical activity is of little value as a means of recognition.

The specific gravities of the essential oils mostly range between 0.850 and 0.990; but some few have a density below 0.850, and others, especially the oxygenated and sulphuretted oils (oils of bitter-almonds, wintergreen, mustard, &c.), are heavier than water, the density in some cases reaching to 1.180. The specific gravities of some essential oils are liable to considerable variations with the age of the samples and other conditions.

The essential oils are all readily combustible. They are insoluble, or nearly so, in water, but distinct traces of some of them pass into solution, the water acquiring the characteristic taste and odour of the oil.[1] In alcohol they are freely soluble, and are reprecipitated from their solutions by dilution with water. The separation, however, is rarely, if ever, complete. The essential oils are miscible in all proportions with fixed oils, oil of turpentine, petroleum-spirit, and carbon disulphide, and may be separated from aqueous liquids by agitation with these solvents.

The essential oils are altered or destroyed by treatment with strong nitric or sulphuric acid. By alkalies they are affected according to the nature of their constituents. Thus esters are saponified, phenols and acids are dissolved, and many other constituents (as citral) are affected in a complex manner.

On cooling natural essential oils, the solid principles forming the stearoptenes often crystallise out.[2] On distilling an oil thus freed from bodies of low melting-point the more volatile hydrocarbons first pass over, and on raising the temperature the remainder of the stearoptene may also be obtained in some cases, the non-volatile residue consisting of resin. The more volatile portion of the distillate may be freed from oxygenated

verted into terpenes and esters respectively. The second stage he regards as coincident with the period during which the respiratory energy is brought to bear on the processes of assimilation, when the quantity of oxygen fixed is sufficient to convert the primary alcohols into aldehydes and the secondary into ketones.

[1] Dragendorff states that 1 litre of water holds in solution the following quantities of essential oils: Oil of cloves, 1.5 gramme; oil of rosemary, 0.9; oil of lavender, 0.5; oil of peppermint, 0.2; oil of savin, 0.5; oil of copaiba, 0.12; and oil of bitter-almonds, 2.2 grammes.

[2] Schimmel & Co. (*Report*, Oct., 1898) employ a modification of Beckmann's freezing-point apparatus for the determination of the solidifying-point of the oils of anise, fennel, &c.

bodies by re-distillation over sodium, and the hydrocarbons thus obtained pure.

Many volatile oils contain other oxygenated compounds besides camphors and resins, though it is only of recent years, since the application of improved methods of examination, that the frequent occurrence of these bodies has been recognised. It is, in fact, to the presence of such oxygenated constituents that the characteristic aroma, flavour, and medicinal value of many essential oils are chiefly, if not entirely, due, the hydrocarbons having but little value in these respects and acting chiefly as diluents. Hence so-called "terpeneless" or "concentrated" essential oils are now prepared by careful fractional distillation of the crude oils. The terpenes have a lower boiling-point than the valuable alcohols, aldehydes, &c., and hence pass over first, while the fractions of higher boiling-point are more powerful in odour and flavour than the entire oil, owing to the removal of the greater part of the comparatively valueless terpenes.[1]

Since the value of the oxygenated constituents of essential oils has become more generally recognised, methods for determining the proportion present in the oils, and of isolating some of them in an approximately pure state, have come into use, and certain of them have received official recognition in the pharmacopœias of recent date. These analytical methods are described at length in the sequel.

Analysis of Essential Oils.

The isolation or determination of the various constituents of essential oils is often extremely difficult, and not unfrequently impossible. Much advance, however, has been made in this direction of late years, and though no generally-applicable or systematic method of analysis can be prescribed, in many cases it is now quite feasible to ascertain by comparatively simple methods the presence and approximate proportion of the constituent on which the value of an essential oil depends. Thus, by agitating the oil with a solution of caustic alkali, *acids* and *phenoloid bodies* will be dissolved,—as hydrocyanic and benzoic acids from oil of bitter almonds, cinnamic acid from oil of cinnamon, thymol from oil of thyme, &c. By boiling with caustic alkali, preferably in alcoholic solution, any *esters* will undergo saponification. Boiled with caustic soda and lead acetate, the

[1] By careful fractionation, lemon oil can be separated into about 92 to 94 per cent. of limonene and 6 to 8 per cent. of oxygenated bodies (chiefly citral and esters of geraniol). The distillation is necessarily conducted under reduced pressure, since too high a temperature leads to decomposition of some of the oxygenated constituents.

sulphuretted oils (*e. g.*, oils of garlic and mustard) give black lead sulphide. Oils containing aromatic *aldehydes* precipitate metallic silver from an ammoniacal solution of the nitrate. The aldehyde may be separated from the other constituents by agitating the oil with a strong aqueous solution of acid sodium sulphite, when (1) a crystalline compound is formed from which the remaining oil may be separated by agitation with ether; or (2) the crystalline aldehyde-sulphite compound dissolves in the excess of sulphite solution, and the lighter non-aldehydic portion of the oil may be readily separated from the lower layer.

The foregoing classes of constituents having been separated as completely as possible, the chemically indifferent bodies can then be more advantageously dealt with. By cooling the oil thoroughly, many of the *stearoptenes* or so-called camphors may be crystallised out, the hydrocarbons usually remaining fluid. Oil of roses presents an exception, for by cooling from 10 to 20 per cent. of a mixture of crystalline hydrocarbons, said to have the formula C_nH_{2n}, is deposited.

FRACTIONAL DISTILLATION affords one of the simplest and best means of effecting a rough proximate analysis of essential oils. The process should be conducted systematically, and under conditions as little variable as possible. The use of a dephlegmator, as described under "Commercial Benzols" (Vol. II, Part ii), is useful for effecting a sharper separation than is otherwise practicable, but it is undesirable to prolong the operation of distillation longer than is absolutely necessary, since polymerisation or other change is liable to occur by long exposure to a high temperature.

In the analysis of essential oils and allied substances, it is frequently necessary to distil the liquid under examination at a reduced pressure, or even *in vacuo*. For example, in the determination of the citral in lemon oil by Parry's process (page 339), the oil must first be concentrated by distilling off the greater part of the terpenes at a pressure of about 12 mm. In the apparatus shown in figure 1 the distillate drops into a series of test-tubes which can be revolved at will by turning the handle A of the Brühl's jar.

When circumstances permit, it is desirable to employ a flask fitted with Glinsky's bulbs or other form of fractionater, but when the amount of oil available is small, this refinement is impracticable.

An alternative form of apparatus (figure 2) is that recommended by Fischer and Harries (*Ber.*, 1902, xxxv, p. 2158). The glass-tube triangle fitted with four stop-cocks enables the receiver to be changed by letting in air to equalise the pressure, without destroying the vacuum in the apparatus. This ar-

rangement is also more convenient than a Brühl's jar, which takes some time to exhaust.

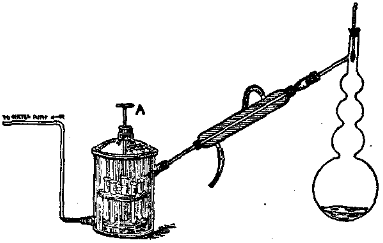


Fig. 1.

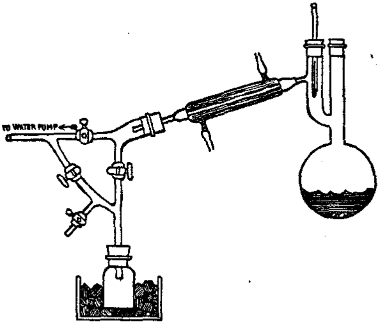


Fig. 2.

Apparatus for Distillation under Reduced Pressure.

Detection of Sulphur Compounds in Essential Oils.

Sulphuretted bodies, such as form the major parts of the oils of garlic and mustard, may be detected by boiling the sample with lead acetate solution and excess of caustic soda, when black lead sulphide will separate.

For the detection of iso-thiocyanates or thiocarbimides, such as exist in oil of mustard, the sample should be boiled with alcoholic caustic alkali, the solution diluted with water, acidulated with hydrochloric acid, and a drop of ferric chloride added. The production of a blood-red colour, due to the formation of ferric thiocyanate, indicates the previous existence of an iso-thiocyanate (thiocarbimide).

Methods for the determination of sulphur compounds in essential oils are fully described under Oil of Mustard (Vol. III, Part iii).

Determination of the Acids in Essential Oils.

The acids may be determined rapidly and with considerable accuracy by dissolving a known weight of the essential oil in neutral methylated spirit, adding a few drops of phenolphthaleïn solution, and titrating the liquid with standard caustic alkali. The operation may be carried out exactly as in the case of fixed oils (Vol. II, Part i).

1 cc. of normal caustic soda required for neutralisation represents:—

0.060 gramme of acetic acid.
0.102 gramme of valeric acid.
0.122 gramme of benzoic acid.
0.148 gramme of cinnamic acid.
0.138 gramme of salicylic acid.
0.164 gramme of coumaric acid.
0.168 gramme of vanillic acid.

Hydrocyanic acid, which is found in bitter-almond oil, cherry-laurel oil, &c., cannot be readily titrated, but may be determined with accuracy by the methods described in Vol. III, Part iii.

Detection and Determination of Phenoloids.

The presence of phenoloids may often be detected by dissolving the sample in alcohol and adding a solution of ferric chloride, which produces a blue or violet coloration. Chavicol, chavibetol, eugenol, and thymol are among the phenoloids which respond to this test.

Phenoloids may be extracted from essential oils containing them by agitating the sample with aqueous caustic alkali. Any free acids present will be dissolved out with the phenols; hydrocyanic acid and benzoic acids from bitter-almond oil, and cinnamic acid from oil of cinnamon, being thus extracted. The process may readily be made quantitative by simply agitating a known measure (*e. g.*, 10 cc.) of the oil with a 5 per cent. solution of caustic alkali in a graduated tube, or a flask

with a narrow neck graduated in divisions of 0.1 cc., observing the decrease in the volume of the oily layer. It sometimes happens that the oily and aqueous strata do not separate sharply, in which case a definite volume of petroleum spirit may be conveniently added. The foregoing process may be employed for the determination of thymol in oil of thyme and eugenol in clove oil.

Determination of Alcohols in Essential Oils.

Alcohols are present far more frequently and in larger proportion in natural essential oils than was formerly recognised. They form the most valuable constituents of the oils of peppermint, geranium, santal-wood, &c. For their determination, it is often convenient to convert them into the corresponding acetic ester by treatment with excess of acetic anhydride, sodium acetate being added to absorb the water formed in the reaction. The resultant ester is then saponified, and the alcohol present calculated from the amount of alkali entering into the reaction.

In order to ascertain the amount of actual "alcohol" in an essential oil, it is often necessary to make a supplementary determination of the esters present. The following details show the application of the method to the analysis of peppermint oil: A weight of 5 grammes of the sample[1] is placed in a strong bottle having a capacity of about 100 cc., and 30 cc. (very accurately measured) of a normal solution (40 grammes of NaHO per litre) of sodium hydroxide in alcohol added. The bottle is then securely closed and kept in a bath of boiling water for one hour. After cooling, the bottle is opened, and the contents titrated, without removing them, with normal or semi-normal acid (sulphuric or hydrochloric), using phenolphthaleïn as an indicator. The percentage of menthol present in the oil in the form of esters will be found by the following formula:—

$$\text{Menthol }\% = \frac{15.6\ (30 - \text{volume of normal acid required for neutralisation})}{\text{Weight of sample employed.}}$$

The neutralised liquid resulting from the previous operation is next thoroughly agitated in a separator with 100 cc. of water. The aqueous liquid is tapped off, and the oily layer, shaken with three successive quantities of water, using about 100 cc. each time, to ensure the complete removal of the alcohol. The washed oil is then carefully separated from the aqueous liquid and transferred to a long-necked flask of a capacity of 100 to 150 cc.

[1] In the case of essential oils comparatively rich in esters a smaller quantity (2 grammes) may be taken, and the process conducted exactly in the manner prescribed for fixed oils (Vol. II, Part i, page 56).

Twenty cc. of acetic anhydride and 2 grammes of fused sodium acetate are then added, and the mixture boiled gently under a reflux-condenser for about an hour. The flask is then cooled, the liquid shaken with 100 cc. of water, and the washed oil treated *very gradually* with a 5 per cent. solution of caustic soda, taking great care to avoid any considerable rise of temperature. This washing with dilute soda solution is repeated until the liquid retains a slight alkaline reaction to litmus even after repeated agitation with the oil. The oil is then washed several times with pure water, separated, dried by contact with potassium bisulphate, and filtered. The acetylised oil thus obtained contains the whole of the menthol of the original sample in the form of menthyl acetate. From three to five grammes should then be saponified by treatment for one hour with 50 cc. of normal alcoholic soda, in a closed bottle or under a reflux-condenser, and then titrated with standard acid, exactly as already described. Then if v represent the volume in cubic centimetres of normal acid required for neutralisation, and a the weight of acetylised oil, the percentage of *total menthol*, free and as esters, contained in the original oil will be found by the following equation:—

$$\text{Total Menthol} = \frac{15.6\ (50 - v)}{a - 0.042\ (50 - v)}$$

F. B. Power, to whom the application of the foregoing process to the assay of peppermint oil is due, states that test experiments on pure menthol show the method to possess remarkable accuracy.

In cases where an alcohol other than menthol is to be determined, one-tenth of the combining weight of that alcohol must be substituted for the constant 15.6 of the above formula.

The U. S. Pharmacopœia (8th Rev.) requires oil of peppermint, as assayed by the acetylisation and ester processes, to show at least 8 per cent. of menthyl acetate and at least 50 per cent. of total menthol (free and as esters).

Haller recommends the following modification of the above process in the examination of the oils of geranium, citronella, peppermint, &c.: The amount of esters is first separately determined, and then a separate portion of the oil is saponified with a suitable amount of caustic potash, so as to obtain the whole of the alcohols in a free state.[1] The product is separated from the aqueous liquid, washed with water, and dried with anhydrous sodium sulphate. The dried liquid is then heated either with succinic or phthalic anhydride, whereby the alco-

[1] In the case of citronella oil, however, the determination of the alcohols by this method includes the citronellal, which is converted into isopulegol by the alkali (pages 334, 335).

hols are converted into mono-ester acids. Strong caustic soda solution is then added to convert these bodies into sodium salts, and the terpenes and other indifferent bodies are then removed by agitation with ether. The pure alcohols are recovered by saponifying the alkaline liquid, and extracting with ether.

Geraniol and *Citronellol* (page 328) can be determined jointly and separately in oils containing them (*e. g.*, oils of geranium, citronella, &c.) by the method described on page 334.

Determination of Esters in Essential Oils.

Esters in essential oils may be readily determined by the saponification process of Koettstorfer employed for the examination of fixed oils (Vol. II, Part i). Certain modifications of the procedure there prescribed are sometimes desirable, such as judicious alterations in the quantity of the sample and in the strength of the alkali and acid used. The details given on page 229 for the determination of the esters in oil of peppermint are applicable to the great majority of cases in which it is required to determine the esters in essential oils.

For the determination of the linalyl acetate in bergamot or lavender oil, Schimmel & Co. recommend that about 2 grammes of the oil should be saponified by heating it on a water-bath for half an hour, in a flask fitted with a reflux-condenser, with 10 cc. of semi-normal alcoholic potash, the liquid being subsequently diluted with water and titrated with semi-normal acid. The amount of *ester* present in the weight of the sample of oil employed for the experiment may be found by subtracting the number of cubic centimetres of normal acid required to neutralise the excess of alkali from the volume of normal alkali employed for the saponification. The difference will be the volume of normal alkali actually required for the saponification of the ester and each cubic centimetre of this corresponds to one combining weight in milligrammes of the ester in question. Thus 1 cc. of normal caustic alkali represents:—

0.088	gramme	of ethyl acetate.
0.152	"	of methyl salicylate.
0.196	"	of linalyl acetate.
0.196	"	of bornyl acetate.
0.198	"	of menthyl acetate.

Determination of Aldehydes and Ketones.

Certain essential oils, as, for instance, the oils of bitter almonds, cassia, cinnamon, citronella, and lemon-grass, are chiefly or largely composed of aldehydes. These may be detected by most of the general reactions for aldehydes (Vol. I), and may conveniently be determined by converting them into

their bisulphite compounds. These crystalline compounds are usually soluble in water, but insoluble, or very slightly soluble, in alcohol, and sparingly soluble in aqueous solutions of bisulphites of the alkali-metals (more readily on warming). (The compounds with barium sulphite are often soluble.) In practice, the essential oil is shaken with excess of a nearly saturated aqueous solution of acid sodium sulphite,[1] the mixture allowed to stand in the cold for twenty-four hours, and the non-aldehydic constituents removed by agitation with ether. The ethereal solution may be evaporated and the residue weighed, the aldehydes being determined by difference. If a direct determination be desired, the crystals of the bisulphite compound are separated from the mother-liquor by pressure between folds of blotting-paper. The compound is then distilled with water and dilute sulphuric acid, or preferably sodium carbonate, and the aldehyde which passes over separated from the water by agitation with ether or chloroform.

The foregoing process is applicable to the isolation of benzoic, cinnamic, salicylic, cumic, and anisic aldehydes, vanillin and piperonal, as well as to the aldehydes of the aliphatic series.

Schimmel & Co. recommend the following mode of applying the bisulphite reaction to the determination of the cinnamic aldehyde in cinnamon oil. Ten cc. of the sample should be placed in a flask of a capacity of 100 cc., and having a long, narrow neck graduated into tenths of a centimetre. From 65 to 70 cc. of a 30 per cent. aqueous solution of sodium acid sulphite ($NaHSO_3$) is then added, and the reagent mixed with the oil by agitation assisted by gentle warming, to promote the solution of the crystalline bisulphite compound which first separates. A further addition of the bisulphite solution is then made, so as to cause the undissolved oil to enter the graduated part of the neck, when its volume is read off. This is subtracted from the 10 cc. of oil operated on to find the aldehyde present. No correction is required, as the cinnamic aldehyde and non-aldehydic constituents of cinnamon oil have approximately the same specific gravity.

The application of the bisulphite process to the determination of citral in lemon oil is attended by peculiar difficulties. These are described fully on page 338, *et seq.* The neutral sulphite process for the determination of aldehydes and ketones (Burgess) is also described on page 342.

[1] Sodium bisulphite is most commonly used, but the potassium salt is stated to be preferable for separating the cinnamic aldehyde from the oils of cinnamon and cassia. Potassium hydrogen sulphite, $KHSO_3$, is however, very unstable and difficult to obtain in a state of approximate purity. It may be conveniently replaced by potassium meta-bisulphite, $K_2S_2O_5$, which occurs in commerce in crystals that are practically pure and fairly permanent.

Certain ketones resemble the aldehydes in forming crystalline addition-compounds with bisulphites. Methyl-heptenone, thujone and pulegone are of this class, but no bisulphite compound is obtainable from camphor, carvone, fenchone, or menthone. The bisulphite compounds of the ketones should be decomposed by distillation with a dilute solution (5 per cent.) of caustic soda or sodium carbonate, and not by dilute sulphuric acid. The application of the bisulphite process to the preparation of thujone from wormwood oil is described on page 380.

Aldehydes and *ketones* may also be isolated by converting them into the corresponding *semicarbazones*, by reaction with semicarbazide.[1]

A solution of semicarbazide is conveniently prepared in accordance with the directions of Thiele and Stange (*Liebig's Ann. Chem.*, cclxxxi, 19) by dissolving together 130 parts of hydrazine sulphate, 55 of sodium carbonate, and 85 of sodium cyanate in 1000 parts of water. A measure of 100 cc. of this solution is treated with 150 cc. of alcohol, and the liquid filtered after standing for several hours. A weight of 10 grammes of the aldehyde to be tested is then added to the clear filtrate. The carbazide crystallises out gradually and the greater part separates in the course of twenty-four hours. The liquid is then filtered and the semicarbazone still in solution precipitated by addition of water and recrystallised from alcohol. The united products are then purified by solution in methyl alcohol and precipitation by water.

Benedikt and Strache (*Monatsh. f. Chem.*, 1893, xiv, 270) have proposed to determine the total amount of *ketones* and *aldehydes* present in an essential oil by ascertaining the carbonyl number or yield of *hydrazone* obtained by treating an alcoholic solution of the sample with phenyl-hydrazine hydrochloride and sodium acetate, used in quantity roughly proportionate to the aldehydic and ketonic bodies present. If the carbonyl number is above 40, from 0.5 to 1.2 gramme of the substance is treated with a weight of phenyl-hydrazine hydrochloride between 1 and 1½ times the weight of the oil. With a carbonyl number between 10 and 40, from 1 to 2 grammes of substance should be employed with from 0.5 to 1 gramme of the reagent. When the carbonyl number is below 10, from 2 to 5 grammes of the sample and 0.5 gramme of the reagent should be used. In any case a quantity of sodium acetate is added equal to 1½ times the weight of

[1] *Semicarbazide*, or carbamic hydrazide, $NH_2.CO.NH.NH_2$, may be prepared by heating a mixture of molecular proportions of urea and hydrazine hydrate for three hours in a sealed tube at 100°. It crystallises in colourless prisms melting at 96°, and reduces Fehling's solution and ammonio-silver nitrate in the cold. When shaken with aldehydes, semicarbazide yields characteristic crystalline compounds (semicarbazones).

phenyl-hydrazine hydrochloride employed, and preferably in 10 per cent. alcoholic solution. The mixture is warmed on the water-bath for a quarter of an hour in a flask holding about 100 cc., and filled about two-thirds full with the alcoholic fluid, whereby too vigorous ebullition is avoided; after cooling, the liquid is diluted to 100 cc. with water, the insoluble matter filtered off through a dry filter, aud 50 cc. of the filtrate oxidised with Fehling's solution. The nitrogen thereby evolved is collected and measured, so as to determine the amount of unaltered phenylhydrazine in the liquid, and thus obtain the data for determining the quantity precipitated as hydrazone. For this purpose a standard solution of phenylhydrazine may be conveniently used in the first instance, containing about 5 per cent., its precise strength being determined by treating a known volume with Fehling's solution. The salt must be free from aniline. The purification of the nitrogen from benzene vapour is necessary when accurate results are desired and is effected by Benedikt and Strache by the arrangement shown in figure 3. The longer end of the U-tube is fixed to a stoppered reservoir, the shorter end being drawn out to a fine point and placed inside the tube containing the nitrogen to be purified. About 200 cc. of alcohol is now allowed to run down from the reservoir so as to spirt upwards in a fine jet into the nitrogen tube; this absorbs all benzene vapour present in the nitrogen. In turn, some 400 cc. of water is similarly passed down from the reservoir to absorb alcohol vapour, after which the measuring-tube is removed to another vessel containing water, and the volume of the nitrogen read off. A number of direct observations with nitrogen, to which benzene was added after measurement, showed that this method of treatment sufficed to remove all benzene vapour within the limits of reading-error.

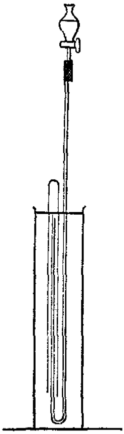


Fig. 3.

A Lunge's nitrometer can be conveniently substituted for the above arrangement.

Duplicate determinations made in this way are stated rarely to differ more than at most one or two units in the value of the carbonyl number deduced, but this value sometimes exhibits a considerable divergence from the actual amount of aldehyde or ketone present. The following figures were obtained with

different samples of oils containing large proportions of aldehydic or ketonic constituents:—

Oil, &c.	Carbonyl Number.	Aldehyde or Ketone Present.	Per Cent. of Aldehyde or Ketone.
Cumin,	51.8	Cuminol, $C_{10}H_{12}O$	47.9
"	45.2	"	41.8
"	96.7	"	89.4
Caraway,	42.0	Carvone, $C_{10}H_{14}O$	39.3
"	33.6	"	31.5
"	38.3	"	35.9
"	61.1	"	57.3
"Carvol,"	84.0	"	78.8
Bitter almond,	147.5	Benzaldehyde, C_7H_6O	97.7
Bitter almond, free from hydrocyanic acid,	147.7	"	97.8
Bitter almond, artificial,	145.3	"	96.2
Cinnamon,	92.7	Cinnamic Aldehyde, C_9H_8O	76.5
"	77.4	" "	63.9
Cassia,	94.3	" "	77.8
"	79.9	" "	66.0

For the preparation of the condensation-products of aldehydes (*e. g.*, geranial) with acetone, in such a manner as to avoid secondary reactions, W. Stiehl recommends the following mode of operating:—

A weight of 50 grammes of the well-dried and freshly-distilled aldehyde is dissolved in 50 cc. of absolutely dry acetone, and the solution cooled down to 0° at least. A weight of 2.5 grammes of sodium is dissolved in 50 cc. of strictly absolute alcohol, and the solution also cooled down to 0°. Finally, 10 grammes weight of tartaric acid is dissolved in 50 cc. of water. The solution of sodium ethylate is then added to the solution of the aldehyde in acetone, the mixture being kept cool and continually stirred, and in fifteen minutes the reaction is interrupted by the addition of the solution of tartaric acid. The acetone and alcohol are then distilled off in a current of steam, and the residual oil is separated from the solution of tartaric acid and washed. The oil thus obtained is distilled with superheated steam and then rectified either under diminished pressure or purified by means of a solution of sodium bisulphite. For this purpose a 50-gramme portion of the crude acetone condensation-product is boiled with 100 cc. of commercial solution of sodium bisulphite, and 100 cc. of water, for about three hours under a reflux-condenser. After the whole is cooled down the small

quantities of substances which are not ketones are carefully removed by agitation with ether, and the bisulphite double-compound decomposed in the cold with caustic soda. The separated oil is well washed, and rectified, first with superheated steam and then under diminished pressure.

O. Doebner (*Ber.*, 1894, xxvii, pp. 352, 2020) has described a reaction which appears to be strictly characteristic of the *aldehydes*, and does not take place with other compounds containing a CO— group, as ketones, lactones, and dibasic acids.[1] The test is applied by treating the aldehyde with molecular proportions of pyroracemic acid (pyruvic acid) and β-naphthylamine, when a crystalline compound is formed having the constitution of an α-alkyl-β-naphthocinchoninic acid. The reaction is applied by Doebner to the detection of citral and citronellal (see pages 336, 337).

Special methods for the determination of citral or geranial, the characteristic aldehydic constituent of lemon-grass and lemon oils, are described on page 338 *et seq.*

Iodine-Absorptions of Essential Oils.

The proportion of iodine which enters into combination when an essential oil is treated in the manner prescribed first by Hübl for *fatty* oils (Vol. II, Part i) is in some cases a valuable indication of the purity of the sample. Unfortunately, the iodine-absorption varies very considerably with the temperature and the time the treatment is continued, and is apparently affected by other more obscure conditions. Barenthein appears to have been the first to employ the iodine-absorption for the examination of essential oils, and he has recorded the results obtained with eleven kinds of oil (*Archiv der Pharm.*, Oct., 1886). It is probable that his results were obtained by the use of an insufficient excess of iodine or by allowing too short a time for the reaction. R. H. Davies and H. W. Snow have also published a number of results (*Pharm. Jour.* [3], xix, 821; xx, 4). Davies allowed the mixture to stand overnight before titrating, while Snow varied the time of action from six to forty hours.

R. A. Cripps (*Chem. News*, 1889, lx, 236) recommends that the reaction should be permitted to continue overnight, a constant time being allowed (eighteen hours), and he points out the differences which result from variations of temperature. To the precautions mentioned by Cripps should be added the

[1] Doebner's reaction occurs in every case tried except that of hydroxy-aldehydes, such as glycerose, in which a hydroxyl-group is linked to the carbon atom to which the aldehydic residue is attached. Doebner considers this an explanation of the fact that sugars which are regarded as having an aldehydic constitution do not respond to the test.

essential condition that the mixture should be excluded from light till ready for titration.

The following table shows the results recorded by the above-mentioned observers for the *iodine-absorptions* of various essential oils:—

Oil.	Observer.		
	Barenthein.	Davies.	Snow.
Aniseed,	164	190	121 (40 hours).
Bergamot,	260	276	345 (40 hours).
Caraway,	265	...	233 (40 hours).
Caraway (English),	...	255	...
Cassia,	...	159	...
Celery,	...	312	...
Chamomile,	...	65	...
Chamomile (English),	...	68; 72	...
Cinnamon,	100	189	...
Cloves (English distilled),	270	349 to 367	467 (40 hours).
Cubebs (English distilled),	...	223 to 227	...
Dill (English),	...	257	...
Fennel,	140	158	...
Juniper (English),	...	337	...
Juniper (Foreign),	245	364	...
Lavender (English),	...	265 to 275	286 (40 hours).
Lavender (French),	170	263 to 294	...
Lemon,	...	328 to 355	343 (40 hours).
Nutmeg (English distilled),	...	309	...
Nutmeg (Foreign),	...	321	...
Orange,	...	...	362 (40 hours).
Pennyroyal,	...	...	152 (40 hours).
Pennyroyal (Foreign),	...	190	...
Peppermint (English),	...	50 to 58	...
Peppermint (American),	...	82 to 144	23 to 88 (6 hours). 24 to 74 (15 hours). 67 to 179 (40 hours).
Peppermint (Japanese),	...	43; 48	64 (40 hours).
Rosemary,	185	...	...
Rosemary (Foreign),	...	325	...
Sandalwood (English distilled),	...	227: 234	...

R. Williams has recorded (*Chem. News*, 1889, lx, 175) the iodine-absorptions (in two hours) of a number of specimens of essential oils, and has also determined the amount of potassium hydroxide required for the neutralisation and saponification of the same samples. Unfortunately, the amount of alkali required for the neutralisation of the free acid of the oils was not determined separately. The free acid present was partly the cause of

the high potash number obtained with bergamot oil. The following table shows the results obtained by Williams:—

Oil.	Iodine Absorbed. (Per Cent.)			Potash-Number. (Parts per 1000.)		
	Sample.			Sample.		
	A.	B.	C.	A.	B.	C.
Aniseed,	274	186	...	2.5	3.8	...
Bergamot,	248	284	...	114.3	87.8	...
Cajuput,	71	151	...	3.5	4.1	...
Caraway,	258	263	...	5.3	3.5	...
Cassia,	75	72	...	101.7	96.2	...
Cedar-wood,	78	75	...	9.2	9.2	...
Cinnamon,	128	105	...	51.3	49.1	...
Citron,	360	320	354	6.7	10.0	13.1
Citronella,	186	191	...	33.5	34.3	...
Cloves,	180	155	...	24.8	23.5	...
Eucalyptus,	62	106	111	5.2	3.6	3.5
Juniper,	273	236	250	11.2	8.4	7.0
Lavender (English),	230	248	233	37.0	31.7	5.2
Lavender (French),	199	237	199	48.5	92.0	49.0
Lavender (Spike),	288	207	...	19.9	7.4	...
Lemon,	323	320	...	14.9	14.1	...
Lemongrass,	223	271	...	22.5	20.1	...
Mace,	221	224	...	8.5	6.7	...
Nutmeg,	202	206	...	3.5	1.9	...
Orange,	348	342	...	3.9	3.8	...
Pennyroyal,	86	78	...	14.6	46.2	...
Peppermint (English),	37	46	...	18.3	19.7	...
Peppermint (American),	72	53	...	43.7	27.1	...
Peppermint (Japanese),	56	37	...	22.9	22.2	...
Rosemary,	162	142	...	7.8	8.8	...
Rue,	192	121	...	5.6	2.9	...
Sage,	50	117	...	70.9	15.8	...
Sassafras,	163	151	...	3.3	2.8	...
Thyme (red),	181	168	...	19.1	10.9	...
Verbena,	268	248	...	12.0	13.7	...

Senglé-Ferrière and Cuniasse have also recorded the iodine-absorptions of a number of essential oils (*Analyst*, 1903, page 217). Simmons (*Chem. and Druggist*, 1904, p. 703) states that the iodine-absorption of pure rose oils ranges from 187 to 194, and that this determination offers the best criterion of the purity of an otto. (See Rose Oil.)

Methoxyl Numbers of Essential Oils.

The determination of the proportion of methyl or equivalent alkyl radical eliminated from the molecule by treatment with hydriodic acid, was proposed by S. Zeisel in 1886 as a method of differentiating essential oils. The process consists in heating the compound with concentrated hydriodic acid, and receiving the alkyl iodide formed in an alcoholic solution of silver nitrate. From the weight of silver iodide produced that of the alkyl radical (in terms of methyl or methoxyl) can be calculated,

since AgI corresponds to CH_3O. Zeisel's method has been somewhat modified by Benedikt and Grüssner (*Chem. Zeit.*, 1889, xiii, 872; abst. *Jour. Soc. Chem. Ind.*, viii, 735), who operate as follows: From 0.2 to 0.3 gramme of the substance is placed in a flask of 30 to 35 cc. capacity, and treated with 10 cc. of hydriodic acid of 1.70 specific gravity.[1] The flask is heated in a bath of glycerin, a current of carbon dioxide being passed through it.[2] The alkyl iodide formed passes through a series of bulbs, the first of which is empty, the second contains water, while the third contains water having purified red phosphorus in suspension.[3] The bulbs are surrounded with water, the temperature of which can be kept, if desired, at 70° C., which heat is necessary in the determination of ethoxyl (C_2H_5O). After passing the bulbs, the alkyl iodide, which is quite free from hydriodic acid and iodine, is absorbed in a flask containing 5 cc. of a 40 per cent. aqueous solution of silver nitrate and 50 cc. of 95 per cent. alcohol. As a precaution, the gas is further passed through a mixture of 1 cc. of the silver solution with 10 cc. of alcohol. The mixed silver solutions are diluted with water, acidulated with nitric acid, and the silver iodide filtered off and weighed.[4] By multiplying the weight found by the factor 0.132 ($= \frac{31}{235}$), the equivalent of methoxyl (CH_3O) may be found.

Instead of weighing the silver iodide, G. Gregor (*J. S. C. I.*, 1898, p. 609) absorbs the alkyl iodide in a solution of silver nitrate of known strength, and subsequently determines the excess of silver in the filtered liquid.

The above methods are evidently inapplicable in the presence of alcohol, but may, on the other hand, be employed for the

[1] Herzig makes an addition of 8 per cent. of acetic acid to the hydriodic acid (*Monatsh. f. Chem.*, ix, 544). The hydriodic acid employed should be free from sulphur and phosphorus compounds, and should be tested by means of a blank experiment.

[2] W. H. Perkin (*Proc. Chem. Soc.*, 1903, p. 239) employs a special form of long-necked distilling flask designed to prevent hydriodic acid from distilling over with the alkyl iodide, which latter is absorbed by impinging on the surface of the liquid in the first flask and by bubbling the gases through the liquid in the second flask.

[3] G. Gregor replaces the red phosphorus and water in the third bulb by a solution of 1 part of arsenious oxide and 1 of potassium carbonate in 10 parts of water. According to W. Kropatschek, the solution of these substances should not be stronger than 1 to 2 per cent. The bulb is liable to become choked with the precipitated arsenious oxide unless refilled for each determination. Not the slightest reduction of the silver nitrate solution in the flask takes place, as in the case when the bulb contains phosphorus.

[4] In the presence of sulphur compounds, a black precipitate is formed in the silver solution, and it is necessary to determine the actual weight of iodine precipitated, instead of merely weighing the precipitate. Or the precipitate may be treated with dilute nitric acid till the silver sulphide is dissolved. A modified process for the determination of the methoxyl-group in compounds containing sulphur has been proposed by F. Kaufler, *Analyst*, 1902, page 126.

determination of alcohol when the true methoxyl-number of the oil is known. Absolute alcohol has the methoxyl-number 674 ($\frac{31 \times 1000}{46} = 674$).

Herzig and Meyer have proposed to differentiate between the methyl radical when attached to oxygen (methoxyl), and when attached to nitrogen (methylimine). They find that, by a suitable modification of Zeisel's process, boiling hydriodic acid liberates the methyl-radical from methoxyl only, while a temperature of 200° to 300° C. is required for the hydrolysis of the methylimine radical. M. Busch, however (*Ber.*, 1902, xxxv, 1565; abst. *Analyst*, xxvii, 251), states that the decomposition of the methylimine radical occasionally occurs when the compound containing it is simply boiled with hydriodic acid. Thus if a negative result be obtained with any compound when boiled with hydriodic acid, the absence of methoxyl may be regarded as proved, but a positive result should not be accepted as conclusive evidence of its presence.

In the case of oils containing esters of higher alkyl-radicals, such as butyl, amyl, and hexyl, the liquid above the silver precipitate does not become clear even if the treatment with hydriodic acid be continued for many hours, since small quantities of alkyl iodides are continually passing over.

NAME OF OIL.	ORIGIN.	METHOXYL NUMBER.	NAME OF OIL.	ORIGIN.	METHOXYL NUMBER.
Anise, ...	Schimmel & Co.	171.1	Cinnamon-leaf, .	...	151.3
Birchwood-tar, ..	...	46.3	Cinnamon, ...	Ceylon oil.	53.1
Cumin, ...	...	17.2	Citron-peel, ...	...	48.8
Cumin (extra strong), ...	...	13.6	Elemi, ...	Schimmel & Co.	25.0
Clove ("Eugenol"), ...	Schimmel & Co.	183.5	Gaultheria, ...	Artificial wintergreen oil. Schimmel & Co.	184.8
Clove, ...	...	152.5	Cherry-laurel, ..	Free from HCy.	28.5
			Olibanum, ...	Schimmel & Co's. frankincense oil.	18.8
			Parsley seed, ..	Schimmel & Co.	190.5

The above table gives the recorded methoxyl-numbers, or milligrammes of alkyl in terms of methoxyl, present in one gramme of various oils. The majority of essential oils, however, contain no oxyalkyl-radical, and hence yield mere traces or no silver iodide when submitted to the process. Among these oils are those of absinthe, bitter-almonds (both natural and artificial), angelica, orange-flowers, copaiba, coriander, cubebs, *Eucalyptus globulus*, Spanish, French, and African oils of geranium, juniper-berries, cherry-laurel, balm-mint, peppermint, rosemary, sage, sandal-wood, turpentine, and valerian.

The results of the examination of different samples of the same kind of oil did not invariably give the same results. Thus two samples of cumin oil gave small methyl-numbers, while two others gave wholly negative results. Similar differences were observed in the cases of the oils of bergamot and citron-peel.

Benedikt and Grüssner point out that the method may be employed for the determination of the eugenol in the oil of cloves, cinnamon, &c., and of anethol in the oils of anise and fennel. 235 parts of silver iodide precipitated correspond to 164 of eugenol, or 148 of anethol.

Optical Activity of Essential Oils.

The great majority of natural essential oils exercise a rotatory power on the plane of polarisation of light, and the optical activity may be ascertained quantitatively by the use of a polarimeter. The instrument employed should be one in which monochromatic light is used, saccharimeters constructed for observing the transition-tint not being suitable for the purpose. The result of the observation commonly recorded is the angle of rotation observed when a column of oil one decimetre in length is traversed by the light. This may be conveniently called the "optical activity" of the oil. Sometimes this observation is calculated to the "specific rotatory power" of the sample by dividing the angle of rotation by the specific gravity of the oil. Not a little confusion has arisen through observers failing to state distinctly on what basis their results are expressed. In this volume all values for optical rotation are to be taken as referring to 100 mm. (one decimetre) of the substance, unless otherwise specified.

The optical activity of an essential oil is one of the most valuable factors in its examination for purity, and this value is accentuated by optical observations on the fractions separated by distillation. Further, an observation of the optical activity of certain of the constituents of essential oils is a valuable criterion of the purity of the substances in question.

Refractive Indices of Essential Oils.

The determination of the refractive indices of essential oils is of considerable value in certain cases, but the figures given by a genuine oil and its adulterants frequently overlap each other to such an extent as to render the factor of little or no use. Still there are many instances in which the specific gravity and optical activity of an essential oil lie close to those of its common adulterants, and in these cases the determination of the refractive index will often give valuable information. Thus, oil of wintergreen has a high and nearly constant refractive

index of about 1.5370 at 20°. Almost any adulterant will be directly detected by the determination of the refractive index of the sample. Sandalwood oil has also a high refractive index (about 1.5050 at 20°), and although adulteration with cedar-wood oil (R. Index, 1.500) could not be recognised by this method, the addition of castor oil would be readily detected.

Other useful applications of the determination will be made when its value is more generally recognised. The observation of the refractive index of the successive fractions yielded by a complex oil on distillation (preferably under reduced pressure), gives much sharper and more definite results than the observation of the index of the untreated sample. Thus, the terpenes have high refractive indices compared with the paraffins and their allies, and the presence of petroleum in essential oils may thus be ascertained. Sesquiterpenes, again, have a very high refractive index, and are thus easily detected in admixture with terpenes. Parry has in this manner recognised the presence of the oil of African copaiba in peppermint oil, and of resin spirit in citronella oil.

A number of determinations by E. J. Parry of the refractive indices of certain essential oils and their characteristic constituents are given in the table on the opposite page. The specific gravity and optical rotation of many of the samples are also added.

A large number of determinations of the refractive index of various essential oils are recorded in a paper by Utz (*Apoth. Zeit.*, 1901, page 742); while H. G. Smith (*Proc. Roy. Soc., N. S. Wales*, 1906, Vol. XXXIX) has recorded the refractive indices of all the known eucalyptus oils (118 species), and based upon the figures obtained a classification of these oils into seven groups.

Adulteration of Essential Oils.

Essential oils are extremely liable to adulteration, the usual sophistications being by addition of oil of turpentine and fixed oils; and by mixing the cheaper essential oils with the more expensive. Alcohol is occasionally met with as an adulterant, and chloroform is said to have been employed. Scientific methods of adulteration are now largely practised, a type of the methods employed being the case of the addition of acetic esters of glycerin to ester-containing oils, and so on. In addition to the above intentional adulterants, volatile oils are apt to contain water and resinous and other oxygenated bodies produced by their exposure to air.

REFRACTIVE INDEX OF ESSENTIAL OILS (PARRY).

OILS.	SPECIFIC GRAVITY at 15°.	OPTICAL ROTATION IN 100 MM. TUBE.	REFRACTIVE INDEX at 20°.	OILS.	SPECIFIC GRAVITY at 15°.	OPTICAL ROTATION IN 100 MM. TUBE.	REFRACTIVE INDEX at 20°.
Aniseed,	0.965	—1.0	1.5541	Lemon	0.859	+58.5	1.4757
Aniseed,	0.987	—0.7	1.5545	Lemon-grass,	0.899	+1.0	1.4862
Bergamot (39 per cent. esters),	...	...	1.4663	Lemon-grass,	0.900	±0.0	1.4855
Cardamom,	...	...	1.4661	Lime (hand-pressed),	0.880	+40.0	1.4840
Caraway,	...	...	1.4870; 1.4807	Lime (hand-pressed),	0.878	+35.5	1.4846
Caraway chaff,	...	...	1.4829	Lime (distilled),	0.859	+39.0	1.4760
Cassia,	...	...	1.5851	Lime (distilled),	0.862	+38.5	1.4770
Cedar-wood,	0.948	—35.0	1.5011	Paraffin (kerosene),	...	...	1.4476
Cedar-wood,	0.947	—33.5	1.5004	Petitgrain,	...	...	1.4623
Citronella,	0.906	—12.0	1.4811	Pimento,	...	...	1.5309; 1.5303
Citronella,	0.909	—10.5	1.4830	Rose,	...	...	1.4619; 1.4609; 1.4615
Clove (B. P.),	1.054	—0.5	1.5306				1.4614; 1.4621
Clove (B. P.),	1.052	—1.0	1.5310	Rue,	...	...	1.4341
Clove (B. P.),	1.056	—0.7	1.5318	Spike Lavender,	0.909	+0.0	1.4670
Clove (90 per cent. eugenol),	...	...	1.5360	Spike Lavender,	0.910	+7.0	1.4666
Clove (light),	...	...	1.5264; 1.5301				
Clove stem,	...	...	1.5322	CONSTITUENTS.			
Coriander,	...	...	1.4694	Anethol,	...	±0.0	1.5606
Eucalyptus (B. P.),	0.917	+2.0	1.4629	Carvone,	...	...	1.4970
Eucalyptus (B. P.),	0.910	—1.5	1.4662	Caryophyllene,	...	...	1.4999
Geranium (French),	...	...	1.4679	Cinnamic Aldehyde,	...	...	1.6068
Geranium (Turkish),	...	...	1.4760; 1.4805	Citral,	...	±0.0	1.4900
			1.4796; 1.4785	Citronellal,	...	...	1.4481
Geranium (East Indian),	...	...	1.4768	Citronellol,	...	...	1.4572
Hop,	...	...	1.4854; 1.4858	Eucalyptol,	0.930	±0.0	1.4582
Lavender (English),	...	...	1.4600; 1.4678	Eugenol,	...	...	1.5412
Lavender (French),	...	...	1.4638; 1.4643	Geraniol,	...	...	1.4792; 1.4799; 1.4766
Lemon,	0.858	+59.0	1.4754	Limonene,	...	+63.0	1.4746
				Phellandrene,	...	...	1.4880

The proportion of *water* in essential oils is never very large. The hydrocarbons in some cases dissolve about 1:1000, but in the oxygenated oils water is more soluble.[1] The presence of water may be detected by mixing 10 cc. of the sample of oil, previously filtered if not perfectly clear, with 40 cc. of petroleum-spirit. Any water will be separated in the form of minute globules, which, if in sufficient quantity, will ultimately coalesce and sink to the bottom of the liquid. On adding a small quantity of plaster of paris, previously gently ignited and weighed, and agitating thoroughly, the water will be absorbed; and on filtering the liquid through dry paper, washing the plaster with a little anhydrous ether or very volatile petroleum-spirit, and drying it at a gentle heat, the increase in its weight will represent the water in the 10 cc. of the sample of oil employed. The petroleum spirit employed for the above test must be previously dehydrated by agitation with plaster of paris.

Alcohol in essential oils may be detected by gradually adding some dry powdered calcium chloride, agitating well, and heating in a water-bath between each addition. Mere traces of alcohol render the first portions of the calcium chloride pasty, but if present in larger proportions the salt dissolves and forms a heavy liquid layer. If the experiment be performed in a graduated tube, and a known measure of the oil employed, the diminution in its volume will give that of the alcohol mixed with it. The calcium chloride should be added until it no longer dissolves in the heavier liquid. In testing for small quantities of alcohol by this test, the oil should be previously dehydrated by agitating it with recently-ignited plaster of paris. Dragendorff recommends the use of metallic sodium, which does not act on hydrocarbons, and but slightly in the cold on oxygenated essential oils, if pure and dry; but in presence of 10 or even 5 per cent. of alcohol a brisk evolution of gas takes place. Aniline-red (magenta) is insoluble in essential oils, if pure and dry, but in presence of a small proportion of alcohol they acquire a pink

[1] H. W. Landbeck (*Pharm. Jour.* [4], xv. 309) points out that commercial essential oils almost always contain small quantities of water, derived from the distillation with steam, and to this moisture is due the formation of more or less hydrogen peroxide, the amount of which varies with the time the oil has been kept. Hence an idea of the age of an oil can be obtained by the intensity of the blue tint it imparts to paper prepared by dipping it in a solution of 1 part of starch and 2 of potassium iodide in 100 of water. The oil to be examined is shaken with an equal quantity of distilled water, and after the water has separated a few drops of it are allowed to trickle on to the prepared paper. If the oil has been recently rectified no blue coloration will be produced. A more accurate criterion of the proportion of hydrogen peroxide could doubtless be obtained by titrating the aqueous liquid with a dilute solution of permanganate, but the amount of peroxide present depends too much on other conditions besides the age of the oil for its determination to have much value in the direction suggested.

or red colour. A colorimetric determination of the alcohol might probably be based on this reaction (see Vol. I). When the proportion of alcohol is considerable, fair quantitative results may be obtained by agitating the oil in a graduated tube with an equal measure of glycerin. The increase in the bulk of the latter liquid, measured after separation is complete, gives that of the alcohol (and water) in the sample examined. If olive oil be substituted for the glycerin, the alcohol (and water), if present in sufficient proportion (*e. g.*, 20 per cent.) will form a separate layer. Simple agitation of the oil with water removes the alcohol sufficiently accurately for most purposes.

When the actual isolation of the alcohol is desired, and the proportion is too small to separate on treating the sample with olive oil, E. Barbier recommends that one-tenth should be distilled off and the distillate saturated with an excess of dry potassium acetate, which forms with the alcohol a heavy liquid. This is separated from the layer of oil, mixed with four times its measure of water, and again saturated with potassium acetate to get rid of the last traces of oil. The filtered aqueous liquid may then be distilled to one-half, when the alcohol will be found in the distillate.

Chloroform may be detected by dissolving the oil in alcohol and warming the liquid with zinc and dilute sulphuric acid. After some time several volumes of water are added, the aqueous liquid separated from the oil by passing it through a wet filter, and the filtrate tested for chloride by adding silver nitrate and nitric acid. An affirmative reaction proves the presence of chloroform in the oil. Chloroform may also be detected as described in Vol. I.

The detection and determination of *alcohol* and *chloroform* in essential oils are rendered more delicate and accurate by previously distilling the sample, and applying the tests to the portion which passes over below 100° C. A still better method is to pass a current of steam through the sample of oil contained in a small retort or tubulated flask. Any alcohol or chloroform will be found in the first portions of the distillate. On continuing the operation the essential oils distil over, though their boiling-points are considerably above 100°, and after a time little or nothing but *resinous matters*, or *fixed oils* added as adulterants, will remain in the retort. These may be weighed in the retort, after heating it moderately and passing a current of coal-gas or air (previously filtered through cotton-wool) to separate any condensed steam and unvolatilised essential oils. The nature of the residue can then be ascertained by treating it with alcohol of 0.85 specific gravity. If wholly resinous it will dissolve, but fixed oils remain insoluble, with the exception of *castor oil*. To detect this, the alcoholic solution should be treated with an

equal measure of sodium carbonate solution, and then boiled till the alcohol is driven off. Any *castor oil* will remain as an oily layer, but the *resin* will have dissolved in the alkaline liquid, and may be detected by separating any undissolved oil and acidulating with hydrochloric acid, when a turbid liquid will be formed from which resinous flocks or globules will gradually separate.

Oil of turpentine is readily detected when present in essential oils by a fractional distillation of the sample, and examination of the fraction distilling about 160° C. Pinene, the characteristic constituent of oil of turpentine, may then be recognised by its boiling-point, and by the characters of its nitroso-chloride, &c. In cases where pinene is a normal constituent of the oil, the physical characters of the lightest fractions of the oil will frequently give the clue to its purity or otherwise. The special methods for the detection of turpentine oil are given under the individual essential oils.

Another test for oil of turpentine and other adulterants of essential oils is founded on the solubility of the sample in alcohol, but as this is only a question of degree, and some of the more expensive oils closely simulate the behaviour of oil of turpentine itself, the inferences from the application of the test must be received with caution. Essential oils differ considerably in their behaviour with alcohol, some undergoing solution much more readily than others. These differences are, of course, dependent on the composition of the oils, and hence will not be strictly constant for different samples of oil of the same kind. Much depends also on the strength of the alcohol employed and the temperature at which the experiment is conducted.[1]

Instead of observing the number of measures of alcohol of a certain strength which are required to effect solution of an essential oil (see next paragraph), a preferable plan is to dissolve the sample in strong alcohol and then determine the volume of dilute alcohol (H. Hager, *Year-Book Pharm.*, 1882, p. 239) or water (E. Dowzard, *J. S. C. I.*, 1898, p. 1175) required to occasion turbidity. Dowzard directs exactly 5 cc. of the oil to be mixed with 10 cc. of alcohol of 0.799 specific gravity at 15° C., and water then added gradually from a burette until the liquid becomes turbid. The end-reaction is stated to be very distinct, although some of the more readily-soluble oils show an opalescence before the liquid becomes distinctly turbid. The measure of water in centimetres required to produce turbidity is multiplied by 100, and the product termed the "solubility value" of the oil. Dowzard

[1] The alcohol test for essential oils has been exhaustively reported on by Dragendorff, whose original papers (*Pharm. Jour.* [3], vi. pp. 541, 581, 641, 681, and 721) should be consulted.

records the solubility values, specific gravities, and optical rotation of various oils.

The following table shows the number of cubic centimetres of alcohol of three different strengths required to dissolve 1 cc. of various essential oils at the ordinary temperature. The figures are given on the authority of Schimmel & Co., except when the name of Bush & Co. is given in parenthesis:—

Oil.	Volumes of Alcohol Required for Solution.		
	70 per cent.	80 per cent.	90 per cent.
Angelica root (Bush & Co.)...	..	Above 10	..
Ambrette (Bush & Co.),..........	..	Above 10	..
Angostura bark,..	..	Above 10	
Asarum canadense,.........	2	..	..
Bergamot,........	..	1.5 to 2	..
Buchu (*B. Betulina*),..........	..	..	..
Cardamom,......	..	1	..
Cardamom (Bush & Co.),........	3	..	..
Chenopodium frt..	10	..	..
Chenopodium frt., German.......	10 (nearly sol.).		
Citronella,.......	..	10	..
Cloves,..........	2	..	..
Coriander,.......	2¼	..	..
Coto bark (Para),	3	..	..
Cumin,..........	..	7	..
Dill,.............	..	5 to 10	..
Geranium,.......	2 to 3	..	..
Juniper,.........	..	Above 10	..

Oil.	Volumes of Alcohol Required for Solution.		
	70 per cent.	80 per cent.	90 per cent.
Lavender, Flowers,..........	3	..	..
Lavender, Spike,	3	..	..
Lemon-grass,...	2	..	..
Lignaloe,.......	1.8	..	..
Peppermint,....	..	Above 10	..
Petit-grain,.....	..	2	..
Petit-grain citronnier,....	..	..	Above 3½
Petit-grain (Bush & Co.).	..	10 (turbid)	1
Pimento,.......	1¼	..	..
Rosemary,.....	..	..	½ to 1½
Rosemary (Bush & Co.).	..	10	..
Rosewood (*Bois de rose femelle*) (Bush & Co.),.	2	..	..
Sandal-wood, E. Indian,....	5	..	..
Summer Savory,	..	..	9
Tansy,.........	3	..	..
Balsam Tansy,..	..	Insoluble	2
Tarragon,......	..	Above 10	..
Thuja,.........	3	..	..
Wormwood,....	sparingly	2	..

The data on page 248 are tabulated from the descriptions of essential oils given in the British Pharmacopœia (1898). The figures are not in all cases justified by the facts.

E. Dowzard has suggested the determination of the viscosity as a means of examining essential oils, and gives the following comparative figures: Lemon oil, 139.6; "citrene" (limonene), 105.8; lime, 177; bergamot, 219.8; orange, 112.5; citronella, 536; rosemary, 320; wintergreen, 261; and sassafras oil, 238.

The colour tests for essential oils are neither numerous nor very characteristic. The following are worthy of mention, but should not be implicitly relied on:—

Concentrated sulphuric acid (2 or 3 drops to 1 of oil) assumes with most essential oils a yellow colour, turning brown, and frequently passing finally to a fine red. Oils of cardamoms, cloves, fennel, anise, cajuput, and laurel produce a violet coloration,

PHARMACOPŒIAL CHARACTERS OF ESSENTIAL OILS.

Oil.	Specific Gravity at 15.5° C.	M. Pt., ° C.	B. Pt., ° C.	Optical Rotation for 100 Mm.	Other Characters.	Chief Constituents.
Anise,	.975 to .990 at 20° C.	10 to 15	...	— slight	Congeals at 10° to 15° C.	Anethol.
Cade,	0.990	...	...	...	Sol. in ether, chloroform, partly in cold, but almost wholly in hot 90 % alcohol.	Cadinene.
Cajuput,	.922 to .930	...	...	...	Bluish-green. Becomes semi-solid with phosphoric acid (sp. gr. 1.75).	Cineol.
Caraway,	.910 to .920	...	...	...	Almost colourless. Odour of the fruit, spicy taste.	Carvone.
Chamomile,	.905 to .915	...	...	...	Blue or greenish-blue when fresh.	Fatty esters.
Cinnamon,	1.025 to 1.035	...	...	...	Pale green with ferric chloride, 50 % combined with sodium sulphite.	Cinnamic aldehyde.
Cloves,	not below 1.050	...	...	...	Blue with ferric chloride. Becomes semi-solid (yellow) with strong ammonia.	Eugenol.
Copaiba,	.900 to .910	...	...	lævo-rotatory	Sol. in 1 part absolute alcohol.	Caryophyllene.
Coriander,	.870 to .885	...	...	...	With 3 parts alcohol 70 % gives clear solution.	Linalol.
Cubebs,	.910 to .930	...	...	...	Colourless, pale green or greenish-yellow.	Cadinene.
Dill,	.905 to .920	...	...	not less than +70°	Pale yellow, odour of the fruit, sweet taste.	Carvone.
Eucalyptus,	.910 to .930	...	...	not more than + or —10°	Semi-solid mass with phosphoric acid (1.75). Negative reaction with nitrite test.	Cineol.
Juniper,	.865 to .890	...	...	...	Sol. in 4 parts 95 % alcohol.	Cadinene.
Lavender,	not below .885	...	...	...	Sol. in 3 parts alcohol of 70 %.	Linalyl acetate.
Lemon,	.857 to .860	...	...	not less than +59°	First 10 % of distillate not different by more than 2° in opt. rotation than original oil.	{ Limonene. Citral.
Mustard,	1.018 to 1.030	...	147.2–152.2	...	First and last portions of distillate have same spec. gravity as original oil (absence of ethyl alcohol and petroleum).	Allyl thiocarbimide.
Nutmeg,	.870 to .910	...	...	...	Evaporated on water-bath leaves no crystalline residue (on cooling). (Absence of concrete oil of nutmeg.)	Myristicin.
Peppermint,	.900 to .920	...	...	...	Sol. in 4 parts alcohol of 70 %. Cooled to —8.3° C. and menthol added gives considerable deposit.	Menthol.
Pimento,	not less than 1.040	...	...	...	Semi-solid mass with equal vol. strong ammonia.	Eugenol.
Pine,	.865 to .870	...	...	—5° to —10°	Not more than 10 per cent. distils below 165° C.	Sylvestrene.
Rose,	.856 to .860 at 30°C.	19.4 to 22.2	...	...	Pale yellow, crystalline, semi-solid oil.	Geraniol; citronellol.
Rosemary,	.900 to .915	...	...	not more than +10°	Sol. in 2 parts of alcohol of 90 %.	Cineol; borneol.
Sandal-wood,	.975 to .980	...	...	—16° to —20°	Clear solution with 6 parts of alcohol 70 %.	Santal alcohols.
Spearmint,	.920 to .940	...	...	...	Sol. in equal volume of 95 % alcohol.	Carvone.
Turpentine,	...	...	160 to 180	...	Sol. in equal volume of glacial acetic acid.	Pinene.

and oil of cinnamon a green coloration changing to blue at the edges.

Fuming nitric acid (5 drops to 1 of oil) gives specially characteristic colorations with oils of mace and nutmeg (blood-red), cubebs (green), copaiba (bluish violet), gaultheria (cherry-red), cinnamon (carmine), myrrh (reddish violet), pimento (blood-red), and pennyroyal (violet).

Solid iodine added to essential oils produces somewhat varying effects, oils consisting chiefly of terpenes giving a very energetic reaction, accompanied by evolution of light and heat, while with other oils nothing of the kind is observable.

Dragendorff (*Pharm. Jour.* [3], vi, 682, 721) has described some vivid colour-reactions obtained by treating 1 drop of various essential oils with 10 to 15 drops of a solution of 1 part of bromine in 20 of chloroform, as also by treating 1 drop of the oil with from 15 to 20 drops of a concentrated solution of hydrochloric acid in alcohol. Dragendorff's tests have not met with general acceptance.

A. C. Chapman has described colour-tests which serve to distinguish eugenol from iso-eugenol (see *Analyst*, 1900, p. 313).

CONSTITUENTS OF ESSENTIAL OILS.

In the following table, the more abundant and commonly-occurring constituents of natural essential oils are shown, but the list must not be regarded as exhaustive. There are a few constituents of certain essential oils, such as methyl alcohol, which do not fall naturally within any of the above-named classes, and the indefinite resinous substances produced by the oxidation of certain oils (*e. g.*, turpentine oil) are not included. On the other hand, certain substances—such as mentho-citronellol, ionone, piperonal, and nitrobenzene—though not constituents of natural essential oils, are closely related thereto, and have therefore been included in the table. No mention is made in the table of the remarkable colouring-matters present in certain essential oils.[1]

[1] The substance to which the blue colour of the oils of chamomile, wormwood, and millefolium is due appears to be common to all blue essential oils, and is characterised by an absorption-spectrum exhibiting three bands in the red and orange. It was called *cærulein* by W. H. Gladstone (*Jour. Chem. Soc.*, 1864). Piesse terms it *azulene*, and states that it boils at 281° to 289°. The name *trichamomillol* has also been suggested for it. Kachler (*Ber.*, 1871, p. 36) regards the colouring-matter as a polymer of camphor of the formula $C_{30}H_{48}O_3$. By treatment with potassium it is reduced to a hydrocarbon boiling at 250° to 255°.

TABLE OF CONSTITUENTS OF ESSENTIAL OILS.

Constituent.	Reference Page.	Formula.	Specific Gravity at 15.5° C.	M. Pt. ° C.	B. Pt. ° C.	Chief Sources: Oil of:—
Hydrocarbons.						
Paraffins,	254	C_nH_{2n+2}	. .	. .	. .	*Pinus Sabiniana*, rose, &c.
Cymene,	255	$C_{10}H_{14}$	0.860	. .	175	Wild thyme, nutmeg, turpentine, &c.
Cinnamene,	60; 254	C_8H_8	0.925 at 0°	. .	144	Liquid storax.
Terpenes,	256	$C_{10}H_{16}$	0.848 to 0.880	. .	156 to 185	Turpentine, bergamot, lemon, &c.
Sesquiterpenes (Cedrenes),	275	$C_{15}H_{24}$	0.895 to 0.935	. .	255 to 275	Cedar, cloves, cubebs, &c.
Polyterpenes,	278	$(C_5H_8)n$	. .	. .	. .	(Caoutchouc).
Olefinic Terpene-Alcohols.						
Geraniol,	328	$C_{10}H_{17}$. OH	0.883 to 0.885	. .	230	Geranium, rose, palmarosa, &c.
Linalol,	330	$C_{10}H_{17}$. OH	0.870 to 0.875	. .	198	Linalol, bergamot, lavender, &c.
Citronellol,	332	$C_{10}H_{19}$. OH	0.862	. .	225	Citronella, rose, geranium, &c.
Mentho-citronellol,	350	$C_{10}H_{19}$. OH	0.8315 at 20°	. .	95 to 105 at 7 mm.	Artificially from menthone.
Nerol,	444	$C_{10}H_{17}$. OH	0.880	. .	225 to 227	Neroli, petitgrain.
Cyclic Terpene-Alcohols.						
Borneol,	343	$C_{10}H_{17}$. OH	. .	203 to 204	212	Borneo & Ngai camphor, oils of lavender, rosemary, &c.
Terpineol,	346	$C_{10}H_{17}$. OH	0.9057 at 20° (solid)	35	218	Lovage, cardamoms, valerian; synthetically from turpentine oil.
Terpin,	347	$C_{10}H_{18}$. $(OH)_2$	. .	102	256	Basil, cardamoms, oxidation of turpentine oil.
Cineol[1] (Eucalyptol),	348	$C_{10}H_{18}$: O	0.930	—1 to —3	176	Eucalyptus, cajuput, wormseed.
Menthol,	350	$C_{10}H_{19}$. OH	0.890	42	212 to 215	Peppermint.
Sabinol,	. .	$C_{10}H_{15}$. OH	0.9432 at 20°	. .	208 to 209	Savin.
Myristicol (?),	436	$C_{10}H_{16}O$	0.913	. .	212 to 218	Mace, nutmeg.
Sesquiterpene Alcohols,	353	$C_{15}H_{25}$. OH	. .	. .	. .	Sandal-wood, cedar-wood, &c.

[1] Cineol is not a true terpene-alcohol; it has apparently the constitution of a *cinyl oxide*.

Aromatic Alcohols.						
Benzyl Alcohol,	56	$C_6H_5 . CH_2 . OH$	1.0507	..	204.7	Peru balsam, cherry-laurel, jasmine, ylang-ylang.
Saligenol,	93	$C_6H_4 . (OH) . CH_2 . OH$	..	82	..	By reduction of salicylaldehyde.
Anisyl Alcohol,	..	$C_6H_4 . (OCH_3) . CH_2 . OH$	..	45	259	Flowers of *Cratægus Oxyacantha.*
Phenols & Phenolic Ethers.[2]						
Thymol,	354	$C_{10}H_{13} . OH$	1.028	50	232	Thyme, horsemint, ajowan, &c.
Carvacrol,	381	$C_{10}H_{13} . OH$	0.981	Solidifies at —25°	237	*Origanum hirtum*, satureja, &c.
Chavicol,	358	$C_9H_9 . OH$	1.035 at 20°	..	237	Betel.
Methyl-chavicol,	357	$C_9H_9 . OCH_3$	0.979 at 11.5°	..	215 to 216	Sweet basil, bay, chervil.
Chavibetol,	358	$C_9H_8 . (OCH_3) . OH$	*1.067 at 15°*	..	*254 to 255*	*Dried betel.*
Anethol,	358	$C_9H_9 . OCH_3$	0.986 at 25°	22.5	232 to 234	Anise & star-anise, fennel, &c.
Eugenol,	359	$C_9H_8 . (OCH_3) . OH$	1.072 at 14.5°	..	252	Clove, allspice, cinnamon-leaf, &c.
Methyl-eugenol	357	$C_9H_8 . (OCH_3)_2$	1.041 at 11°	..	248 to 249	Hazel-wort, citronella.
Safrol,	359	$C_9H_8 . O_2 . CH_2$	1.108	11	233	Sassafras, Japanese camphor, &c.
Apiol,	364	$C_9H_6 . (OCH_3)_2 . O_2 . CH_2$	..	30 to 32	294	Parsley-fruit.
Diosphenol,	365	$C_9H_{14} . OH . COH$	..	82	232[3]	Buchu.
Asarol,	364	$C_9H_7 . (OCH_3)_3$	1.165 at 18°	62	295 to 296	Hazel-wort, matico.
Aldehydes.						
Furfural,	..	$C_4H_3O . COH$	1.163	..	161	Cloves.
Citral (Geranial),	335	$C_9H_{15} . COH$	0.899	..	228 to 229	Lemongrass, lime, &c.
Citronellal,	337	$C_9H_{17} . COH$	0.880	..	205 to 210	Citronella, lemon, *Eucalyptus citriodora*, &c.
Benzoic Aldehyde,	24	$C_6H_5 . COH$	1.0504	26	179 to 180	Bitter-almonds, peach, cherry-laurel, &c.
Cinnamic Aldehyde,	44	$C_8H_7 . COH$	1.0497 at 20°	..	130 at 30 mm.	Cinnamon, cassia.
Salicylic Aldehyde,	93	$C_6H_4 . (OH) . COH$	1.172	..	196.5	*Spiræa* oils, &c.
Anisic Aldehyde,	94	$C_6H_4 . (OCH_3) . COH$	1.126	—4	245 to 248	Artificial hawthorn perfume.
Vanillin,	107	$C_6H_3(OH) . (OCH_3) . COH$	..	80 to 81	285	Vanilla, gum benzoin, Peru balsam.
Piperonal (Heliotropin),	114	$C_6H_3 . O_2 . CH_2 . COH$	..	37	263	Artificial heliotrope perfume.
Cuminic Aldehyde,	416	$C_6H_4 . (C_3H_7) . COH$	0.9832 at 0°	..	237	Cumin, caraway, &c.

[2] Under this heading might be included para-cresol-methyl-ether, $C_6H_4 . CH_3 . OCH_3$, which occurs in ylang-ylang oil; guaiacol, $C_6H_4 . OH . OCH_3$, the presence of which in birch-tar oil gives it the odour of Russia leather; and creosol, $C_6H_3 . CH_3 . OCH_3 . OH$, also present in birch-tar oil. This oil and its constituents are, however, fully described in Vol. II, Part ii.

[3] Boils with decomposition.

TABLE OF CONSTITUENTS OF ESSENTIAL OILS (Continued).

Constituent.	Reference Page.	Formula.	Specific Gravity at 15.5° C.	M. Pt. ° C.	B. Pt. ° C.	Chief Sources: Oil of:—
Aldehydes—(*Continued*).						
Aromadendral,	423	$C_{10}H_{14}O$	0.9477	..	210	Certain Eucalyptus oils.
Santalal,	..	$C_{15}H_{24}O$	0.9793	..	..	Sandal-wood.
Ketones and Camphors.						
Methyl-amyl-ketone,	412	$C_5H_{11} . CO . CH_3$	0.837 at 50°	..	151	Cloves.
Methyl-nonyl-ketone,	366	$C_9H_{19} . CO . CH_3$	0.8295 at 17°	15 to 16	224 to 225	Rue.
Methyl-heptenone,	366	$CH_3 . CO(C_3H_5) : (CH_3)C . CH_3$	0.850 at 20°	..	170 to 174	Lemongrass, citronella, linalol.
Carvone,	380	$C_{10}H_{14}O$	0.960 at 18°	..	224	Caraway, fennel, dill, &c.
Fenchone,	378	$C_{10}H_{16}O$	0.9465 at 19°	5 to 6	192 to 193	Fennel, thuja.
Thujone (tanacetone),	380	$C_{10}H_{16}O$	0.9126 at 20°	..	203	Thuja, tansy, absinthe.
Pulegone,	379	$C_{10}H_{16}O$	0.9323 at 20°	..	221 to 222	Pennyroyal.
Laurel Camphor,	367	$C_{10}H_{16}O$	0.990	175	204	Camphor, feverfew, &c.
Menthone,	350	$C_{10}H_{18}O$	0.897	..	206	American peppermint, &c.
Irone,	366	$C_{13}H_{20}O$	0.939 at 20°	..	144 at 16 mm.	Orris root.
Ionone,	392	$C_{13}H_{20}O$	0.9351	..	126 to 128 at 12 mm.	Artificial violet perfume.
Eudesmol,	423	$C_{10}H_{16}O$	..	79 to 80	270 to 272	*Eucalyptus macrorhyncha*, *E. capitellata*, *E. camphora*, &c.
Free Acids and Anhydrides.						
Benzoic Acid,	13	$C_6H_5 . COOH$	..	121.5	249	Ylang-ylang, also in gum benzoin, Tolu & Peru balsams.
Cinnamic Acid,	39	$C_8H_7 . COOH$	1.247	133	300	Liquid storax, Tolu & Peru balsams.
Salicylic Acid,	64	$C_6H_4 . (OH) . COOH$	..	155 to 156	..	Wintergreen, birch, &c.
Coumaric Acid,	49	$C_6H_4 . (OH) . (CH)_2 . COOH$	..	195	..	*Melilotus officinalis*, &c.
Coumaric Anhydride (Coumarin),	48	$C_6H_4 . O . (CH)_2 . CO$	..	67	290	Tonka bean, woodruff, *Melilotus*, &c.
Esters.						
Methyl Salicylate,	87	$CH_3 . C_7H_5O_3$	1.187	..	220 to 224	Wintergreen, *Betula lenta*, &c.
Benzyl Acetate,	..	$C_6H_5 . CH_2 . C_2H_3O_2$	..	..	106	Jasmine.
Linalyl Acetate,	331	$C_{10}H_{17} . C_2H_3O_2$	0.8951 at 20°	..	99 to 105 at 15 mm.	Bergamot, lavender, jasmine.
Geranyl Acetate,	329	$C_{10}H_{17} . C_2H_3O_2$	0.9174	..	242 to 245	Indian geranium, lemon, &c.

Esters—(*Continued*).						
Bornyl Acetate,	346	$C_{10}H_{17} . C_2H_3O_2$	0.991	29	98 at 10 mm.	Pine-needles, thyme, golden-rod, &c.
Bornyl Valerate,	346	$C_{10}H_{17} . C_5H_9O_2$	0.956	..	255 to 260	Valerian.
Menthyl Acetate,	447	$C_{10}H_{19} . C_2H_3O_2$	..	..	223	Peppermint, &c.
Geranyl Tiglate,	425	$C_{10}H_{17} . C_5H_7O_2$	..	..	..	Geranium.
Alkyl Tiglates & Angelates,	410	....	..	..	..	Roman Chamomile.
Methyl Anthranilate,	437; 444	$C_6H_4 . (NH_2) . CO . O . CH_3$	1.168	25	132 at 14 mm.	Neroli, jasmine, orange lime flowers.
Sulphuretted Compounds.						
Dimethyl Sulphide,	386	$(CH_3)_2S$	..	..	..	American peppermint.
Vinyl Sulphide,	386	$(C_2H_3)_2S$	0.9125	..	101	*Allium ursinum.*
Allyl Iso-thiocyanate (thio-carbimide),	386	$C_3H_5 . NCS$	1.018	..	148	Black mustard-seed, rape-seed.
Butyl (Secondary) Iso-thio-cyanate,	386, 387	$CH(CH_3) . C_2H_5 . NCS$	0.944 at 12°	..	160	*Cochlearia officinalis.*
Acrinyl Iso-thiocyanate,	386	$C_7H_7O . NCS$	..	..	..	White mustard-seed.
Phenyl-ethyl Iso-thiocyanate,	386	$C_2H_4(C_6H_5) . NCS$	..	..	..	Mignonette-root.
Nitrogenised Compounds.						
Hydrocyanic Acid,	27	HCN	0.697 at 18°	..	26.5	Bitter-almond, cherry-laurel.
Benzaldehyde-cyanhydrin,	27	$C_6H_5 . CH(OH) . CN$	..	..	..	Bitter-almond, cherry-laurel.
Trimethylamine,	..	$N(CH_3)_3$	..	..	35	Chenopodium.
Pyrrol,	..	$C_4H_4 : NH$	0.9752 at 12.5°	..	131	Derivatives in orange oil from unripe fruit.
Indol,	..	$C_6H_4 : (CH)_2 : NH$	..	52	245[1]	Jasmine.
β-phenyl-propionitrile,	..	$C_6H_5 . C_2H_4 . CN$	..	..	261	Watercress (*Nasturtium officinale*).

[1]Boils with decomposition.

The majority of the bodies classified in the foregoing tables are described at length in the sequel. The more important of the acids occurring in essential oils have already been treated in the chapter on "Aromatic Acids," together with such of their aldehydes, alcohols, and esters as are of natural occurrence or practical interest. The aldehydes and esters of linalol and geraniol are described in the section on "Olefinic Terpene-Alcohols." Descriptions of the more important of the nitrogenised compounds occurring in essential oils will be found in other volumes.

HYDROCARBONS OF ESSENTIAL OILS.

Of the hydrocarbons occurring as constituents of the essential oils of plants, by far the most abundant and numerous are the *terpenes* and their immediate allies. The properties and chief sources of these hydrocarbons will be fully described in the sequel. *Paraffins* occur in a few cases only. Thus the "*abietene*" of the oil of *Pinus sabiniana* (California) is identical with *normal heptane*, C_7H_{16} (Pt. ii, page 22). The stearoptene or solid portion of oil of rose appears to consist of the paraffin *hexadecane*, $C_{16}H_{34}$, mixed with other substances. The hydrocarbons of the *benzene* series are only rare constituents of the essential oils, with the exception of *cymene*, $C_{10}H_{14}$. *Cinnamene* or *styrol*, a hydrocarbon having the constitution of a *phenylethylene*, $C_6H_5.CH: CH_2$, occurs in small proportion in liquid storax.

By far the most numerous and important of the hydrocarbons of essential oils are the polymers of *pentine*, C_5H_8. The relationship existing between these hydrocarbons is shown by the following arrangement, which is substantially that of Wallach:—

A. Pentines or Hemiterpenes, C_5H_8; as isoprene and valerylene.

B. Dipentines or Terpenes, $(C_5H_8)_2$ or $C_{10}H_{16}$; including pinene, limonene, fenchene, camphene, phellandrene, &c.

C.—Tripentines or Sesquiterpenes, $C_{15}H_{24}$; as cedrene and cubebene.

D.—Diterpenes, $C_{20}H_{32}$; as colophene and copaivene.

E.—Polyterpenes, $(C_5H_8)_n$; as the polyprene of caoutchouc.

Pentines. Hemiterpenes.

Eight bodies of the composition C_5H_8 can theoretically exist, assuming that the formulæ are all open chains.

Isoprene, which is the most interesting of the hemiterpenes,

has probably the constitution of a β-methyl-crotonylene (*i. e.*, unsymmetrical methyl divinyl), $CH_2:(C.CH_3).CH:CH_2$, and hence belongs to Group III of the acetylene series (see Part ii of this volume). It is obtained, together with other products, by the dry distillation of caoutchouc and gutta-percha. It is a volatile liquid boiling at about 37° C., and is not affected by treatment with mercuric bromide and water. By careful management, W. A. Tilden obtained from isoprene a tetra-bromide, $C_5H_8Br_4$, as a yellowish oily liquid which was decomposed on distillation. When isoprene is heated to about 280° C. for some hours it polymerises with formation of *dipentene*, $C_{10}H_{16}$, and colophene, $C_{20}H_{32}$. Isoprene behaves similarly with sulphuric acid, yielding a terpene and a fluorescent colophene.

On exposure to the air, isoprene absorbs oxygen and becomes converted into a white syrupy substance, which on distillation suddenly changes, often with explosive violence, into a white amorphous mass of the composition $C_{10}H_{16}O$. Another characteristic reaction of isoprene is that of being converted into true caoutchouc or india-rubber when brought into contact with certain chemical agents, such as strong hydrochloric acid or nitrosyl chloride.[1] Tilden has also observed the spontaneous polymerisation of isoprene (obtained from turpentine oil) into india-rubber, the inducing cause being possibly the formation of acetic or formic acid by the oxidising action of the air, the acid thus produced converting the remainder of the isoprene into caoutchouc.

Cymene. $C_{10}H_{14}$; or, $C_6H_4(CH_3)(C_3H_7)$.

Cymene is a member of the benzene series of hydrocarbons, and has the constitution of a *para-methyl-isopropyl-benzene*. It cannot be made to combine with hydrogen to form terpenes, though the converse reaction can generally be effected by careful oxidation of the terpene with iodine.[2]

Cymene is the principal constituent of the oil from wild thyme (*Thymus serpyllum*), in which it occurs with thymol and smaller quantities of carvacrol and a terpene. Cymene is present in smaller proportion in the essential oils of ginger, nutmeg, citron, ajowan, cumin, thyme (*T. vulgaris*), sage, *Origanum*

[1] Tilden has pointed out (*Chem. News*, xlvi, 120) that this reaction would have considerable practical interest if isoprene were more readily obtainable.

[2] C. R. A. Wright found that by treatment with bromine or iodine, and subsequent distillation alone or with aniline, most of the terpenes were converted into cymene, and that they all yielded *a-cymene*, and not isomeric varieties of that hydrocarbon. The sesquiterpenes, $C_{15}H_{24}$, also yielded cymene by similar treatment.

creticum and *Satureja hortensis* (pepper-wort). It also occurs in resin-spirit and in old oil of turpentine.

Cymene is formed in considerable quantity by treating turpentine oil with sulphuric acid, and still more abundantly (together with ether) by heating turpentine oil with ethyl sulphate[1] (*Compt. rend.*, xc, 1428). Cymene was first obtained from Roman cumin oil (*cuminum cyminum*) in which it occurs with *cuminol* or *cumic aldehyde* $(CH_3)_2CH.C_6H_4.COH$.

Cymene is a colourless, strongly-refracting fluid, having an agreeable odour, recalling that of oil of lemons. It boils at 175° to 176° C., and has a density of 0.86 at 15° C. When boiled in a flask for thirty or forty hours with a large excess of strong chromic acid mixture, or until the liquid dropping from the inverted condenser no longer appears oily, cymene is oxidised with formation of acetic, paratoluic, and terephthalic acids. To detect the last product, which is characteristic, the contents of the flask are diluted with water and thoroughly cooled. The insoluble terephthalic acid is filtered off, and purified by solution in ammonia, boiling with animal charcoal, and reprecipitation by hydrochloric acid. It is insoluble in water, alcohol, ether, chloroform or acetic acid. It sublimes without fusing. Heated with excess of soda-lime, it yields benzene and a carbonate.

According to C. R. A. Wright, the presence of cymene in an essential oil may be detected by mixing it very gradually with twice its volume of strong sulphuric acid, so as to avoid all heating. After standing twenty-four hours the acid is diluted with water, and the oily liquid separated and distilled in a current of steam. If the oily portion of the distillate blackens when shaken with sulphuric acid, the above treatment should be repeated. The product is then oxidised by chromic acid mixture (see above), when terephthalic acid will be obtained if cymene be present.

Terpenes. Dipentines. $C_{10}H_{16}$; or, $(C_5H_8)_2$.

The terpenes are leading constituents of the majority of the essential oils of plants, in many of which they exist in greater or less proportion. Terpenes are also obtainable by the dehydrolysis of the oxygenated bodies of the composition $C_{10}H_{18}O$ contained in various natural essential oils.[2]

[1] Cymene is conveniently prepared by mixing camphor and phosphorus pentoxide in molecular proportions and heating gently till reaction commences ($C_{10}H_{16}O + P_2O_5 = C_{10}H_{14} + 2HPO_3$). The flask is then cooled, the cymene poured off from the metaphosphoric acid, heated again with phosphorus pentoxide, and then distilled several times over sodium.

[2] Isoprene, C_5H_8, readily polymerises, with formation of a terpene. An

The terpenes are all isomerides of the molecular formula $C_{10}H_{16}$. With the single exception of camphene (solid) they are colourless liquids, lighter than water and usually volatile without decomposition. They distil unchanged in a vacuum or a current of steam. The terpenes present a close similarity in their physical properties, a fact which renders their isolation and differentiation extremely difficult. This difficulty is further increased by the tendency which the terpenes exhibit as a class to pass from one into the other under very slight provocation, and by the ability of some of them to exist in several different physical modifications. As a result, the earlier investigators seldom obtained exactly the same product from two different botanical sources, and this circumstance led to the supposed discovery of innumerable terpenes, which were generally named by adding the suffix *ene* to one of the botanical names of the plant from which the oil had been obtained. Personal equation, in the details of the method of preparation, further led to different descriptions being given to the product from the same plant.

A marked advance in the knowledge of terpenes and their allies was made by Berthelot, who observed that the terpene of American turpentine oil rotated the plane of a ray of polarised light to the right, while the terpene of French turpentine oil was lævo-rotatory. Tilden and Shenstone further distinguished between the terpenes of the *pinene*-group, $C_{10}H_{16}$, boiling at 156° to 160° C., constituting the chief constituents of the essential oils of the *Coniferæ* and *Labiatæ*, and the "citrenes" (now called limonenes), boiling at about 175°, constituting the greater part of the oils from the *Aurantiaceæ* and *Umbelliferæ*. In the meantime, the crystalline additive-compounds formed by the terpenes with hydrochloric acid had been studied, and Tilden and his collaborators had discovered the interesting compounds of the terpenes with nitrosyl chloride (NOCl) and nitrogen trioxide. At this point, O. Wallach commenced the remarkable researches which, in conjunction with those of Brass, Conrady, Bruhl, Baeyer, Otto and Gildemeister, and others, have, since 1884, placed the knowledge of the terpenes and their allies in a new light, and rescued their chemistry from the previous confusion. These remarkable results were for the most part obtained by the study of the action, on the terpenes and their

optically-inactive hydrocarbon of the formula $C_{10}H_{16}$, having most of the characteristic properties of the natural terpenes, has been obtained by the action of alcoholic potash on dibrom-rutylene. Another body of the same composition has been synthetically obtained from amylene (*Ber.*, xviii, 838). A *dihydro-cymene*, which has the constitution of a *methyl-isopropyl-dihydrobenzene*, and is possibly identical with *terpinene*, has been obtained. It is a liquid which boils at about 174° C., smells like turpentine oil, and resinifies on exposure to air. It decolorises permanganate and forms an uncrystallisable bromide.

allies, of water, of the halogens and their hydrogen compounds, of oxidising agents, of nitrous acid and nitrosyl chloride, and of the compounds which the products of the action of the last two reagents formed with bases.

A further remarkable achievement in the domain of synthetical chemistry has been made by W. H. Perkin, Jun., by his syntheses of dipentene, terpineol, terpin hydrate, and carvestrene (*J. C. S.*, 1904, lxxxv, 654; *Proc. C. S.*, 1906, xxii, 268).

The method employed for observing the behaviour of terpenes with acidulated alcohol is described on page 274, and the formation of the hydrochlorides on pages 265 to 268.

The formation of the *bromides* is best observed by dissolving 1 volume of the terpene in 4 volumes of alcohol and 4 of ether. The solution is well cooled by ice, and then 0.7 volume of bromine is slowly added. The crystalline precipitate is washed with cold alcohol and recrystallised from ether.

The *nitroso-chlorides* of the terpenes were originally obtained by W. A. Tilden by the action on the oils of nitrosyl chloride gas, whereby compounds of the formula $C_{10}H_{16}NOCl$ were obtained. A more convenient method is that of Wallach (*Annalen*, ccxlv, 241), who mixes 14 cc. of the terpene (pinene, limonene, sylvestrene)[1] with 20 cc. of amyl nitrite and 34 cc. of glacial acetic acid. This mixture is well cooled, and half its measure of a mixture of equal volumes of glacial acetic and fuming hydrochloric acids gradually added, allowing time for the blue coloration to disappear before adding more of the mixed acids. The *nitroso-bromides* may be obtained in a similar manner.

On treating the terpene nitroso-chlorides with alcoholic potash or cautiously heating them alone, the elements of hydrochloric acid may be removed, and products of the composition $C_{10}H_{15}NO$ obtained.

By treating the terpenes with nitrogen trioxide, *terpene nitrosates* are formed of the composition $C_{10}H_{16}NO(ONO_2)$. Wallach prepares such compounds by treating a well-cooled mixture of equal volumes of the terpene and amyl nitrite with ½ volume of glacial acetic acid and one volume of nitric acid of 1.4 specific gravity.

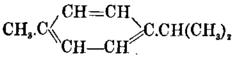
On warming the nitroso-chlorides of the terpenes with excess of piperidine, aniline, or benzylamine, in alcoholic solution, a series of bases are formed which are applicable to the differentiation of the terpenes.

Constitution of Terpenes.

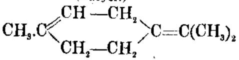
The constitutional formulæ of the terpenes have been the subject of much controversy and ingenious speculation. The

[1] Camphene does not form a nitrosochloride.

CYMENE.

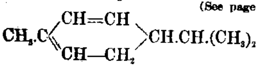


TERPINOLENE.
(Baeyer.)

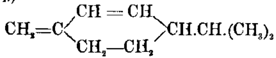


PHELLANDRENE.
(Wallach.)
(See page 274.)

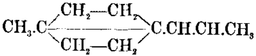
α-Variety.



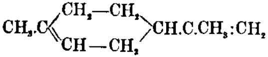
β-Variety.



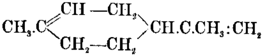
TERPINENE.
(Bruhl.)



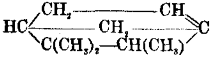
LIMONENE.
(Semmler.)



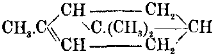
DIPENTENE.



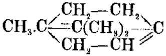
PINENE.
(Tiemann.)



PINENE.
(Semmler.)

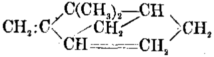


PINENE.
(Bredt.)



CAMPHENE.
(Bredt.)

CAMPHENE.
(Wagner.)



question is still at issue, and hence the formulæ given must merely be regarded as representing those accepted at the present time, according to some of the best authorities.

The foregoing formulæ assume the existence of a benzene-nucleus in the molecule of the terpenes. While cymene undoubtedly contains a typical aromatic nucleus, and hence is related to benzene, the terpenes do not exhibit the stability of the benzene-derivatives, and are now generally regarded as belonging to a group of compounds occupying a position intermediate between the aliphatic or open-chain compounds and bodies of the benzene series. Hence the terpenes have been termed the *alicyclic group*, in recognition of the fact that while containing a closed carbon-chain they approach the aliphatic compounds in their chemical behaviour. Parry prefers the term *hydro-aromatic.*

It will be observed that the formulæ for pinene and camphene show only one ethylene-linkage, whereas in the formulæ of limonene, dipentene, and terpinolene there are two such linkages. The formulæ of phellandrene and terpinene show the close analogy of these two terpenes. The molecular structure of the terpenes profoundly affects their chemical characters, and allows of their convenient classification as follows:—

Group A. *Pinene* forms a compound with hydrochloric acid which is converted by the elimination of the acid into *camphene* and not into pinene. Pinene forms a well-defined dibromide, but no tetrabromide, or only an extremely unstable compound of that nature. *Camphene*, obtained as above, yields a mono-hydrochloride from which it can be recovered unchanged. *Fenchene* appears to belong to this group.

Group B includes *limonene*, *cinene* or *dipentene*, *sylvestrene*, *carvestrene*, and *terpinolene*. These terpenes form characteristic crystallisable tetrabromides. They are apparently true dihydrocymenes.

Group C. *Phellandrene* and *terpinene*, the terpenes of this group, form with nitrogen trioxide crystallisable compounds of the formula $C_{10}H_{16}.N_2O_3$.

Thujene has not been studied sufficiently to allow of its being assigned with certainty to any one of the above classes.

The following table, showing the general characters of the terpenes and their principal derivatives, is based on one by W. A. Tilden (*Watts' Dict. Chemistry*, iv, page 663):—

[1] So-called terpinolene dihydrochloride is very probably cinene dihydrochloride.

[2] If the melting-point recorded for this compound is correct, it points to a difference between cinene and inactive limonene.

[3] The specific rotation of this compound is $[a]_D$, + 183.5°.

[4] Carvestrene, a terpene prepared artificially from carone, is probably inactive sylvestrene. It gives a blue colour with sulphuric acid and acetic anhydride. W. H. Perkin, Jun., has recently described its synthesis.

	Pinene.	Camphene.	Fenchene.	Limonene.	Cinene or Dipentene.	Sylvesthene.	Terpinolene.	Terpinene.	Phellandrene.	Thujene.
Specific Gravity, ...	0.858 to 0.860 at 20° C.	0.8422 at 54°	0.864 at 20°	0.846 at 20°	0.845 at 20°	0.848 at 20°	...	0.847 at 20°	0.8558 at 10°	0.840 at 15°
Specific Rotation, $[a]_D$, ...	+ and —	+80.6°	0	+ and — 105° to 107°	0	+66.3 [4]	0	0	±17.6°	...
Refractive Index, ...	1.4655 at 21° C.	—	1.4690	1.4746	1.4731	1.4747	...	1.4846	...	1.4714
Boiling-point; ° C.	156	158.5 to 159.5 m. pt. 51 to 52°	160	176	178	176	185	180	170 to 172	172 to 175
Monohydrochloride, $C_{10}H_{16}.HCl$, ...	saturated; crystalline, m. p. 125° C.	crystalline; m. p. 152°	liquid.	unsaturated; liquid.	unsaturated; liquid.	liquid.	...	...	...	...
Dihydrochloride, $C_{10}H_{16}.2HCl$, melting-point, °C.,	50	...	...	50	50	72	50 [1]	...	...	...
Dibromide, $C_{10}H_{16}Br_2$, melting-point, ° C., ...	169	90	liquid.	...	...	...	69	liquid.	...	...
Tetrabromide, $C_{10}H_{16}Br_4$, melting-point, ° C., ...	...	...	liquid.	104	125 to 126 [2]	135	116	liquid.	...	...
Nitrosyl-chloride, $C_{10}H_{16}.NOCl$, melting-point, °C,	103 116° (Tilden)	no compound.	...	100 to 106	103 to 104	106	...	...	...	...
Nitrous derivative:— Formula, ... Melting-point, ° C., ...	$C_{10}H_{15}NO$ 132	... ...	... ...	$C_{10}H_{14}N.OH$ 72	$C_{10}H_{14}N.OH$ 93	... ...	... ...	$C_{10}H_{16}N_2O_3$ 155	$C_{10}H_{16}N_2O_3$ [3] 103 to 104	... ...
Benzyl-nitrolamine, $C_{10}H_{16}(NO)NH.C_7H_7$, melting-point, ° C., ...	122	...	...	93 (a)	109 (a)	71	...	137	...	...
Chief sources or modes of formation, ...	Turpentine and juniper oils (*Coniferæ*); sage oil (*Labiatæ*); also in lemon oil, &c.	Isomerisation of pinene. Reduction of camphor and borneol.	Reduction of fenchone from fennel oil.	Oils of neroli, orange-peel, lemon, lime, and bergamot (*Aurantiaceæ*); oils of dill and caraway, (Umbelliferæ), &c., &c.	Isomerisation of other terpenes; elemi, turpentine and other oils.	Russian and Swedish turpentine oils (*Coniferæ*).	Isomerisation of other terpenes.	Isomerisation of other terpenes.	Fennel oil, certain eucalyptus oils.	Artificially from thujone, contained in thuja oil.

Footnotes referred to in this table are inserted at bottom of page 260.

In addition to the reactions described in the table, the terpenes all undergo polymerisation by treatment with a limited quantity of strong sulphuric acid, and form camphoric acid and hydrogen peroxide under the influence of warm water and air.

Proof of polymerisation of a terpene by sulphuric acid is obtained by washing the product with water and distilling it. As the polymers boil at a much higher temperature than the original hydrocarbon, the observation of a thermometer immersed in the vapour affords proof of the change. As the polymerising action of the acid may be incomplete, it is desirable to observe the boiling-points of the less volatile fractions of the altered oil.

The production of hydrogen peroxide may be observed by treating the oil with an equal bulk of warm water, agitating in a capacious bottle with air, allowing the oil and water to separate, and testing the latter liquid for the characteristic product of the reaction. The most delicate test is the formation of brown manganese dioxide on immersing in the liquid a paper soaked in solution of manganous sulphate mixed with acetate of sodium; the bleaching of a paper previously blackened by moistening with a weak solution of lead acetate and exposing it to sulphuretted hydrogen; and the blue coloration imparted to ether when a few cubic centimetres of that liquid and a minute trace of chromic acid are added to the liquid supposed to contain hydrogen peroxide, and the whole agitated.

The terpenes are broken up by oxidation into acetic, oxalic, terebic, and terpenylic acids, and by further treatment into carbonic and acetic acids; but when pure they yield neither toluic nor terephthalic acid. In cases where traces of these acids have been obtained, their production must be attributed to the presence of traces of cymene in the terpene operated upon.

PINENE. $C_{10}H_{16}$. (See also pages 259, 261.)

Pinene forms the most important constituent of French and American oils of turpentine. As prepared from the former source, it was called by Berthelot *terebentene*, and this name may be conveniently employed to designate the pinene of French turpentine oil. This variety of pinene is lævo-rotatory, while the pinene from American oil usually exhibits dextro-rotation. This difference in optical properties extends to the various compounds and polymers of the pinenes from French and American turpentine oils. Where two physical isomerides of a substance exist, the optical activities of the two varieties are usually equal and opposite. The specific rotation commonly assigned to lævo-pinene is —40.4° (—43.4° being the greatest activity observed), while pinene from American oil of turpentine is stated to have a specific rotatory power of + 21.5° for the sodium

ray. From these figures it would appear that one or other of the pinenes is not a homogeneous substance. J. H. Long has proved this to be the fact with respect to the product from American turpentine oil, which is a very variable mixture of dextro- and lævo-pinene, in which the former variety usually predominates, though occasionally the lævo-pinene is in excess. By carefully selecting the crude turpentines, Long obtained from the spruce-pine a lævo-pinene having a specific rotatory power of —40.1° to —42.5°. As the separation of the two varieties of pinene by fractional distillation is impossible, the method commonly employed to obtain dextro-pinene from American turpentine oil is fallacious.

In addition to forming the main portion of French oil of turpentine, *lævo-pinene* occurs in the oils from *Pinus picea* and *P. sylvestris*, together with lævo-limonene and dipentene; in oil of olibanum, with a little dipentene and an unknown oxygenated body; and in oil of rosemary to the extent of 80 per cent., together with cineol, dextro- and lævo-borneol, and dextro- and lævo-camphor. The oils of thyme, sage, and anise also contain lævo-pinene.

Besides forming the greater part of American oil of turpentine, together with variable proportions of lævo-pinene and some dipentene, dextro-pinene also occurs, together with a sesquiterpene, in oil of galbanum; and, in association with an unknown oxygenated body, in the oil from *Daucus carota*.[1]

Lævo-pinene or *Terebentene*, as obtained by a long series of fractional distillations from French turpentine oil, is a colourless mobile liquid of marked and characteristic odour. It has a specific gravity of 0.8767 at 0°/0° and 0.8619 at 17.9°/17.9° (Riban). It boils at 156.5° C.

Dextro-pinene or *Australene*, which forms the leading constituent of American turpentine oil, has the same specific gravity,[2] boiling-point, and chemical characters as the pinene from the French oil, differing from the latter substance solely in the direction of its optical rotation. Eucalyptene, laurene, massoyene, and olibene are mixtures of terpenes containing more or less pinene.

It is very difficult if not impossible to obtain perfectly pure pinene from natural essential oils. A chemically pure substance

[1] Pinenes also form notable proportions of the oils from the Guayana laurel, mace, sweet flag, cheken leaves, and bay leaves. Pinenes exist in smaller proportions in a great number of essential oils, including those from the juniper berry, Russian turpentine, *Pinus pumilio*, laurel, massoy, citron, fennel, myrtle, sage, valerian, hazel-wort, and eucalyptus.

[2] According to W. A. Tilden, dextro-pinene from American turpentine oil has the following specific gravity:—0°/4° = 0.8765; 25°/25° = 0.8586; 100°/100° = 0.8278.

closely resembling the natural pinenes, but optically inactive, is obtained by heating pinene nitroso-chloride with aniline:—

$$\underset{\text{Pinene Nitroso-chloride}}{C_{10}H_{16}NOCl} + \underset{\text{Aniline.}}{2C_6H_5 . NH_2} = H_2O + \underset{\text{Amido-azo-benzene.}}{C_6H_5N_2 . C_6H_4 . NH_2} + \underset{\text{Pinene.}}{C_{10}H_{16}} + HCl.$$

Pinene is nearly insoluble in water and aqueous liquids, but dissolves with facility in strong alcohol, and is miscible in all proportions with ether, chloroform, carbon disulphide, hydrocarbons, and fixed oils.

Pinene distils unchanged at 155° to 156° under the ordinary atmospheric pressure, and is readily volatile in a current of open steam. When heated in a sealed tube for several hours to about 300°, pinene yields a product formerly called *iso-terebentene*, which is so oxidisable that it is converted into a viscid mass on exposure to the air for a few hours. Iso-terebentene consists largely of dipentene, together with terpinene, terpinolene, and polymers of pinene. When the vapour of pinene or ordinary turpentine oil is passed through an iron tube heated to dull redness, a portion suffers conversion into the *isomers* dipentene, terpinene, and terpinolene; a second part is polymerised to "*colophene*"; a third suffers decomposition into hydrogen and *cymene*, $C_{10}H_{14}$; while a fourth portion splits up into two molecules of *isoprene*, C_5H_8 (W. A. Tilden). A notable amount of *meta-xylene* is also formed.

On treatment with a *small* proportion of sulphuric acid, pinene yields an optically-inactive liquid which is a complex mixture of dipentene with variable proportions of terpinene, terpinolene, cymene, colophene, and a mixture of semi-solid products of high boiling-points. The more volatile portions of the product constitute the article commercially known as "*terebene*" (which see).

By treatment with concentrated sulphuric acid *in excess*, pinene is converted into *diterpene* or *colophene*, $C_{20}H_{32}$, with great rise of temperature, some cymene being also formed.[1] Colophene is also produced by treating pinene or turpentine oil with a very small proportion of boron fluoride, and still more highly condensed polymers can be obtained by the action of antimonious chloride.

The action of air and other oxidising agents on pinene is described under "Turpentine oil" (page 475).

Pinene is an unsaturated body, and combines with the halogens, hydracids, nitrosyl chloride, &c., to form definite additive-compounds. The combination is, however, attended with intramolecular change, and hence unaltered pinene cannot be regenerated from the compounds formed.

Pinene Monohydrochloride. Pinyl Chloride. $C_{10}H_{16}$, HCl; or,

[1] According to C. R. A. Wright, a small percentage of cymene is a normal constituent of turpentine oil.

$C_{10}H_{17}Cl$. When dry hydrochloric acid gas is passed into cooled pinene or turpentine oil, either pure or diluted with benzene or carbon disulphide,[1] the gas is rapidly absorbed with formation of a crystalline substance which may be separated by pressure and purified by recrystallisation from alcohol or ether. The product is commonly called *pinene mono-hydrochloride,* but as it is not possible to regeuerate pinene from it, its formation is apparently attended with internal molecular change. Hence the name *pinyl chloride* is to be preferred.

Pinyl chloride crystallises from alcohol or benzene in white feathery needles. It so closely resembles common camphor in appearance, odour, and the property of subliming readily at ordinary temperatures, that it has sometimes been called by the inappropriate name of "artificial camphor," and is apocryphally stated to have been used to adulterate true camphor. Lævo-pinene hydrochloride from French turpentine oil has a specific rotation of —32.2°, but that from the American oil is more or less dextro-rotatory. In either case the compound melts at 131° (J. H. Long and Riban) or, according to Wallach, at 125°, and boils at about 210° with only slight decomposition.

Pinyl chloride is insoluble in water. It dissolves in alcohol, but the solution gives no precipitate with silver nitrate. Pinyl chloride is unaffected by alkalies at the ordinary temperature, but when heated under pressure with alcoholic potash or dry soap, or preferably with an alcoholic solution of sodium acetate and caustic soda, it loses the elements of hydrochloric acid, and yields *camphene* (page 266).

When once formed, pinyl mono-hydrochloride is incapable under any circumstances of taking up a second molecule of HCl, but if turpentine oil be left for some time in contact with concentrated hydrochloric acid, or if a solution of pinene or turpentine oil in ether, alcohol, or acetic acid be saturated with hydrochloric acid gas, a compound containing $C_{10}H_{16}.2HCl$ is formed. This substance, however, is not a pinene compound, but consists of *cinene* or *dipentene dihydrochloride* (page 271).

CAMPHENE. BORNYLENE.[2] $C_{10}H_{16}$. (See also pages 259, 261.)

Camphene is the only solid terpene definitely known. It

[1] According to Wallach, these diluents are superfluous if the liquid be thoroughly cooled and free from any trace of moisture. J. H. Long obtained as good a yield and as pure a product when the pinene was allowed to reach a temperature of 30° C. as when cooled by a freezing mixture, hut the crystals separated more slowly (*J. A. C. S.*, 1899, xxi, 638).

[2] Bornylene is also the name given by Wagner and Brykner (*Ber.*, 1900, xxxiii, p. 2121) to a new terpene obtained in admixture with camphene, when bornyl iodide is heated to 170° in an autoclave with strong alcoholic potash. The bornylene thus produced melts at 98° and boils at 150° C.

exists only rarely in nature,[1] but it is of importance from its relation to pinene, borneol, and camphor.

Camphene occurs among the products of the action of concentrated sulphuric acid on turpentine oil, and is an important constituent of the so-called "terebene."

Pure camphene may be prepared from pinyl chloride (page 265) by heating it with potassium stearate or dry soap to 200° or 220° C. It is also readily obtained by heating equal weights of pinyl chloride and anhydrous sodium acetate, to 200°, for several hours, with twice their weight of glacial acetic acid; or by simply boiling a mixture of pinyl bromide and glacial acetic acid under a reflux-condenser.

Camphene may also be prepared by warming bornyl chloride, $C_{10}H_{17}Cl$, with an equal weight of aniline, and then heating the mixture to about 180°. The formation of aniline hydrochloride occurs suddenly, aud the reaction is complete in a few minutes. When cold, the product is treated with hydrochloric acid, and the camphene distilled off in a current of steam. Camphene is also produced when *bornylamine*, $C_{10}H_{17}NH_2$, is heated with acetic anhydride. Ammonia is split off in the reaction, leaving camphene.

When prepared from pinyl chloride or bromide, the camphene obtained exhibits an optical rotation of the same kind as that of the original pinene, but the product from bornyl chloride is optically inactive.

Camphene is a white solid resembling camphor or paraffin-wax. It has a peculiar odour suggesting that of camphor. The specific gravity of camphene in the solid state is about 0.860. It melts at 51°,[2] and boils at 160°. Camphene is insoluble in water, but dissolves in alcohol, ether, and benzene. It crystallises from its concentrated alcoholic solution in feathery leaflets.

Camphene readily unites with hydrochloric acid to form a camphoroid body melting at 157°, which is probably identical with *bornyl chloride*. The product differs from pinyl chloride by dissociating into camphene and hydrochloric acid by distillation, or more gradually by mere contact with water.

In contact with bromine, camphene is gradually converted into the substitution-product $C_{10}H_{15}Br$. Camphene is generally stated not to form an addition-product with bromine, but according to Reychler, a *camphene dibromide* can be obtained in prisms exhibiting double refraction and melting at 90°.

No nitroso-chloride of camphene appears to exist.

By treatment with oxidising agents, such as chromic acid

[1] According to Bruhl, a camphene is probably present in the oils of myrtle and rosemary. E. J. Parry states that camphene occurs to a small extent in citronella, ginger, and camphor oils.

[2] Or, according to Wallach, at 48° to 49° C.

mixture, camphene is converted into *camphor*, $C_{10}H_{16}O$, which exhibits an optical activity of the same kind as that of the camphene from which it was derived.

The constitution of camphene is still an open question. Two of the more probable formulæ are shown on page 259.

FENCHENE. $C_{10}H_{16}$. (See also pages 261 and 378.)

Fenchene does not appear to occur naturally. It is formed by the reduction of *fenchone*, $C_{10}H_{16}O$, the camphor of fennel oil, to which fenchene bears the same relation that camphene does to laurel-camphor. The fenchone is first reduced to *fenchyl alcohol*, $C_{16}H_{17}.OH$, which is then converted into the hydrochloride, and this body on heating with aniline yields fenchene. Fenchene also results when fenchyl alcohol is strongly heated with acid potassium sulphate. Fenchene forms a liquid monohydrochloride and an oily dibromide which has not been obtained pure. Fenchene resists the action of nitric acid to a remarkable extent. Wallach's researches have shown that fenchene is probably a mixture of two or more isomeric modifications.

LIMONENE. $C_{10}H_{16}$. (See also pages 259 and 261.)

Limonene is a very frequent constituent of essential oils, and some of the oils from the *Aurantieæ* are almost wholly composed of it. Besides occurring largely in these oils, limonene exists largely in the oils of some of the *Umbelliferæ*. Thus it forms about 60 per cent. of oil of dill, and is not much less abundant in oil of caraway, being in each case associated with carvone. The oil from *Erigeron Canadense* is stated to consist almost entirely of limonene, which also occurs in appreciable quantity in some pine oils, in massoya oil (from the bark of *Cinnamomum kiamis*), and in the oil from jaborandi leaves.

The terpenes known as *citrene*, *bergamene*, *hesperidene*, *carvene*, &c., are merely limonene containing traces of impurities varying with the origin of the oils from which they are prepared. To these very persistent impurities the characteristic odours of the oils are frequently due.

The limonene in the oils from the *Aurantieæ* and caraway oil is chiefly dextro-rotatory ($[a]_D = +106.8°$), and the large proportion in which it is present imparts this character to these oils; but the limonene of the oils distilled from the leaves of *Pinus sylvestris* and *P. picea* (known in commerce as "Pine-wool oil") is lævo-rotatory to an almost equal extent ($[a]_D = -105°$). The oils of lemon, lime and caraway contain a mixture of the two limonenes. By mixing equal parts of dextro- and lævo-limonene, an optically inactive terpene is obtained,

which appears to be identical with dipentene. Hence this is generally regarded as a racemoid modification of limonene, but there is some evidence that the two bodies are distinct. (See further, page 271.)

Limonene is a liquid of pleasant odour, boiling at 175° to 176°, and having a specific gravity of 0.846 at 20° C. Hence it is lighter and has a higher boiling-point than pinene.

By oxidising limonene at low temperatures with nitrogen peroxide, dextro-rotatory *limonenol*, a secondary alcohol, is produced, which yields a ketone by further oxidation. This ketone forms an oxime apparently identical with the carvoxime from carvone.

Limonene Hydrochloride, $C_{10}H_{16}$,HCl. On passing a stream of dry hydrochloric acid gas through absolutely dry limonene only one molecule of the acid is absorbed, and *limonene monohydrochloride* is formed. This compound is an optically-active liquid, which on treatment with moist hydrochloric acid is converted quantitatively into inactive *cinene* or dipentene dihydrochloride, melting at 50°, and identical with the compound obtained by a similar process direct from dipentene (page 271). Pinene when similarly treated only yields the solid monohydrochloride melting at 125° C. (See page 265.)

Limonene Tetrabromide, $C_{10}H_{16}Br_4$, is obtained by acting with bromine on limonene dissolved in ten parts of glacial acetic acid. It separates in hemihedral rhombic crystals, which are soft and pliable, and when recrystallised from ethyl acetate melt at 104°. The crystals are more soluble in ether than dipentene tetrabromide (which, moreover, melts at 124°) and the solution is dextro-rotatory.[1] Pinene when treated in the above manner yields a dibromide melting at 169° to 170°.

The foregoing reactions point to the presence of two double (ethylenc) bonds in the molecule of limonene. (See page 259.)

Limonene Nitrosochloride, $C_{10}H_{16}$,NOCl, is obtained by passing nitrosyl chloride into a solution of limonene or oil of orange-peel in five parts of methylated spirit, cooled to —10° C. It may also be conveniently prepared by Wallach's method, described on page 258. The compound separates in crystals which melt at 103°. By boiling with alcoholic potash it is converted into *carvoxime*, $C_{10}H_{14}$(N.OH).

The nitrosochloride prepared from either dextro- or lævo-limonene is always a mixture of two distinct isomerides (α and β), one of which is more powerfully rotatory than the other, and

[1] O. Wallach (*Annalen*, 1891, cclxiv, 1) finds that a liquid isomeride is formed together with the crystalline tetrabromide. On treating the latter compound with alcoholic potash it is converted into a dextro-rotatory compound of the formula $C_{10}H_{13}Br$, which combines with 3HBr to form dipentene tetrabromide.

a separation can be effected by treating the mixture with cold ether or chloroform. In addition to the above four optically-active nitrosochlorides of limonene, an inactive isomeride (dipentene or cinene *α-nitrosochloride*) is formed when equal weights of the α-nitrosochlorides from dextro- and lævo-limonene are mixed in ethereal solution. (See further, page 273.) By similar treatment the limonene β-nitrosochlorides yield cinene β-nitrosochloride.

By warming limonene nitrosochlorides in alcoholic solution with piperidine, aniline, benzylamine, &c., Wallach obtained a series of crystallisable nitrolamines.

The optical rotations and melting-points of these various isomeric derivatives are shown in the following table:—

COMPOUND.	FORMULA.	SOURCE.					
		Dextro-limonene.		Lævo-limonene.		Cinene or Dipentene.	
		Rotation.° $[a]_D$.	Melting-point.	Rotation.° $[a]_D$.	Melting-point.	Rotation.° $[a]_D$.	Melting-point.
Terpene,	$C_{10}H_{16}$.	+106.8	...	—105.00	...	0	...
Monohydrochloride,	$C_{10}H_{16}$. HCl.	—40.	...	+39.5	...	...	...
Tetrabromide,	$C_{10}H_{16}Br_4$.	—73.27	104°	—73.45	104°	0	124°
α-nitrosochloride,	$C_{10}H_{16}NOCl$.	+313.4	103–104°	—314.8	103–104°	0	101°
β-nitrosochloride,	$C_{10}H_{16}NOCl$.	+240.3	105–106°	—242.2	100°	0	...
α-nitrolpiperidine,	$C_{10}H_{16}NO.N(C_5H_{10})$.	+67.75	94°	—67.60	94°	0	154°
β-nitrolpiperidine,	$C_{10}H_{16}NO.N(C_5H_{10})$.	—60.48	111°	+60.18	110°	0	152°
α-nitrolaniline,	$C_{10}H_{16}NO.NH$ Ph.	...	112°	...	112°	0	125°
β-nitrolaniline,	$C_{10}H_{16}NO.NH$ Ph.	...	153°	...	153°	0	149°
α-nitrolbenzylamine,	$C_{10}H_{16}.NO.NH(C_7H_7)$.	+163.8	93°	—163.6	93°	0	110°
α-nitrolbenzylamine hydrochloride,	$C_{10}H_{16}NO.NH(C_7H_7)HCl$.	—82.26	...	+83.06	...	0	...
Carvoxime,	$C_{10}H_{14}.NOH$.	—39.34	72°	+39.71	72°	0	93°
Benzoyl-carvoxime	$C_{10}H_{14}.NOBz$.	—26.97	...	+26.47	...	...	...

The various nitrolamines from dextro- and lævo-limonene unite to form inactive cinene derivatives, in a

manner similar to the nitrosochlorides from the same sources. Thus when equal quantities of the α-dextro- and lævo-nitrolpiperidines melting at 94° are dissolved in petroleum-spirit and the solutions mixed, a sparingly soluble inactive nitrolpiperidine melting at 154° is at once precipitated. A similar inactive compound melting at 152° is obtained by mixing the solutions of the β-nitrolpiperidines. Similar inactive bases are yielded by the aniline and benzylamine derivatives.

CINENE. DIPENTENE.[1] INACTIVE LIMONENE. $C_{10}H_{16}$.

This terpene has been found *abundantly* in but few of the natural essential oils. It is stated to form a considerable proportion of elemi oil, in which it exists with phellandrene and traces of polyterpenes and oxygenated bodies. Wallach also found dipentene or cinene in considerable quantity in the essential oil of the camphor-tree, and according to Brühl, it also occurs in oil of cascarilla. The oils of bay, turpentine, cardamoms, massoya, mace, bergamot, fennel, and myrtle are also stated to contain more or less dipentene; but in view of the facility with which certain other terpenes (especially pinene) are converted into dipentene by the action of heat, acids, &c., the presence of dipentene in essential oils which have been exposed to slightly abnormal conditions is only to be expected. It seems highly probable that the loss in optical activity observed in some oils by storing or heating is frequently due to the formation of inactive dipentene.

Dipentene or cinene, formerly called *terpilene* or *terpinylene*, may be obtained artificially by various reactions. It is identical with Berthelot's *iso-terebentene*, produced with other isomers by heating oil of turpentine to about 250° to 270°, and hence is present in Swedish and Russian turpentine oils, which are prepared from pine-wood tar. Dipentene is likewise identical with *cajeputene*, obtained by heating cajuput oil with phosphoric

[1] The name *dipentene*, though now very generally adopted for the racemoid modification of limonene, is not, in the opinion of the author, well-chosen. It was first suggested by Wallach, who obtained a hydrocarbon probably identical with it by the polymerisation of valerylene, C_5H_8, a homologue of acetylene, C_2H_2. A hydrocarbon of the formula $C_{10}H_{16}$ may be appropriately termed dipentine or divalerylene; but dipentene would be expected to contain two additional atoms of hydrogen. The inconsistency resulting from similar anomalous nomenclature is exhibited by the following examples from Roscoe and Schorlemmer's *Treatise on Chemistry* (Vol. III, Part 5):—

Dipentene,	$C_{10}H_{16}$
Dipentene tetrabromide,	$C_{10}H_{16}Br_4$
Dipentenyl oxide (cineol),	$C_{10}H_{18}O$
Dipentenyl alcohol (terpineol),	$C_{10}H_{17}.OH$
Dipentenylene glycol (terpin),	$C_{10}H_{18}(OH)_2$
Dipentenylene chloride,	$C_{10}H_{18}Cl_2$

anhydride, and with the *cinene* obtained by a series of reactions from cineol (page 350). *Caoutchene*, produced by the distillation of caoutchouc and gutta-percha, also consists essentially of dipentene, which likewise results from the dehydration of terpin, terpineol, and cineol (whence the name *cinene*).

W. H. Perkin, jun., has recently synthesised dipentene, starting from pentane tri-carboxylic acid (*J. C. S.*, 1904, lxxxv, 654).

Cinene is conveniently prepared by boiling one part of pinene or limonene dihydrochloride with one part of sodium acetate and two parts of glacial acetic acid for half an hour in a flask furnished with a reflux-condenser. The product, which was originally called terpilene and supposed to be homogeneous, is then distilled with steam, the oil which distils boiled with caustic potash, redistilled, dried, and purified by fractional distillation.

Dipentene is an oil having an agreeable odour. Dipentene and all its compounds and derivatives are optically inactive. Dipentene itself is at once obtained by mixing lævo- and dextro-limonenes in equal proportions, and its derivatives are produced on mixing the corresponding derivatives of dextro- and lævo-limonene. That the products thus obtained are distinct compounds, and not mere mixtures of limonene derivatives of opposite optical activity, is shown by their melting-points and behaviour with solvents. (See page 269.) The facts appear to point strongly to the view that dipentene bears a similar relation to the active limonenes that racemic acid bears to dextro- and lævo-tartaric acids, although there is some evidence that a mixture of *d*- and *l*-limonenes is *not* dipentene.

The derivatives of dipentene present a close analogy to the corresponding derivatives of acetylene and ethylene. Thus:—

Acetylene,	C_2H_2	Cinene or Dipentene,	$C_{10}H_{16}$
Acetylene tetrabromide,	$C_2H_2Br_4$	Cinene tetrabromide,	$C_{10}H_{16}Br_4$
Ethylene dichloride,	$C_2H_4Cl_2$	Cinyl dichloride, (Dipentene dihydrochloride)	$C_{10}H_{18}Cl_2$
Ethylene oxide,	$C_2H_4 : O$	Cineol,	$C_{10}H_{18} : O$
Ethylene glycol,	$C_2H_4(OH)_2$	Terpin,	$C_{10}H_{18}(OH)_2$
Vinyl alcohol,	C_2H_3OH	Terpineol,	$C_{10}H_{17}OH$

The oxygenated derivatives of dipentene (*e. g.*, terpin, terpineol, and cineol) are described at length on page 346 *et seq*.

Cinene or *Dipentene Dihydrochloride*, $C_{10}H_{16}$, 2HCl, is produced by the action of moist hydrochloric acid on dipentene, limonene, or pinene. (See page 265.) It may be conveniently prepared by mixing a solution of dipentene or limonene in glacial acetic acid, with glacial acetic acid saturated with hydrochloric acid gas. Cinene dihydrochloride crystallises from a mixture of alcohol and ether in rhombic plates, having a peculiar odour and melting at 50° C. It is optically inactive, like all dipentene compounds, and is insoluble in water. It boils at 118° to 120° C. at 10 mm. pressure. It dissolves readily in alcohol, but on heating the

solution an oil separates out, consisting of a mixture of cinene and terpinene dihydrochlorides. By the method described on page 271, cinene can be reproduced from the dihydrochloride; but more or less *terpinene* and *terpinolene*, besides *cymene* and small quantities of a *paraffinoid hydrocarbon*, appear to be constant secondary products (Tilden & Williamson, *J. C. S.*, lxiii, 292).

Cinene dihydrochloride is decomposed by boiling with water or alcoholic potash with formation of *cinyl alcohol* or *terpineol*, $C_{10}H_{17}.OH$, isomeric with cineol (page 348).

When cinene dihydrochloride is treated with a drop of a concentrated solution of ferric chloride and the mixture gently heated, a rose coloration is produced, which changes to an intense violet-red, and ultimately to blue. To obtain the reaction, which was first observed by Riban (*Ann. Chim. Phys.*, [5], vi, 37), it is not necessary to prepare the hydrochloride previously, but a few drops of lemon, turpentine, or other oil containing a terpene which yields cinene dihydrochloride on treatment with moist hydrochloric acid (*e. g.*, pinene, limonene) may be stirred in a porcelain capsule with a drop of concentrated hydrochloric acid, and another drop of a strong solution of ferric chloride. As the sesquiterpenes do not form dihydrochlorides, the test may be used to detect pinene and other terpenes in presence of the former compounds.

Cinene or *Dipentene Dihydrobromide*, $C_{10}H_{16},2HBr$, is obtained by saturating glacial acetic acid with hydrobromic acid gas, and adding a solution of limonene or dipentene in glacial acetic acid. The compound separates at once in crystals which melt at 64° and closely resemble the dihydrochloride.

According to Baeyer, the dihydrochloride and dihydrobromide of cinene each exists in two isomeric forms, comparable to maleic and fumaric acids. The usually occurring or *trans*-modification of the dihydrochloride melts at 50°, whereas the *cis*-form prepared from cineol and hydrochloric acid, melts at 25°. Similarly the *trans*-modification of the dihydrobromide melts at 64°, while the *cis*-form, prepared from cineol, melts at 39°. Both forms easily regenerate cinene.

Dipentene or *Cinene Tetrabromide*, $C_{10}H_{16}Br_4$, is obtained by treating dipentene by the process employed to convert limonene into the corresponding compound (page 268). It forms rhombic crystals which never show hemihedral faces. In addition, the crystals are very brittle, and exhibit well-marked striations. Cinene tetrabromide is stated to melt at 125° to 126°, but there is reason to doubt this figure. It is less soluble in ether than the corresponding compound of limonene. The foregoing characters are of service for the detection of cinene. By treatment with sodium acetate and acetic acid, as described on page 271, dipentene may be re-formed from the tetrabromide.

Cinene or *Dipentene a-nitrosochloride*, $C_{10}H_{16}.NOCl$, is formed when equal weights of the *a*-nitrosochlorides from dextro- and lævo-limonene (page 269) are mixed in ethereal solution. On adding a small quantity of methyl alcohol and allowing the liquid to evaporate slowly the cinene nitrosochloride is obtained. The compound melts at 103° to 104° (101° to 102°, Wallach) and is optically inactive. On boiling with alcohol it is converted into inactive *iso-carvoxime*, melting at 93°, identical with that prepared by mixing the lævo- and dextro-carvoximes (page 268).

SYLVESTRENE. $C_{10}H_{16}$. (See also page 261.)

Sylvestrene occurs in Swedish and Russian turpentine oils together with dextro-pinene and hydrocarbons of higher boiling-point.[1] Sylvestrene is a liquid having an odour like that of fresh pine-wood.

Sylvestrene is one of the most stable of the terpenes. It combines with two molecules of hydrochloric, hydrobromic and hydriodic acids, yielding compounds which melt respectively at 72°, 72°, and 66° C. From the crystalline dihydrochloride, sylvestrene may be recovered unchanged by boiling with aniline. *Sylvestrene tetrabromide* forms monoclinic tablets melting at 135°. The *nitrosochloride* is very soluble in chloroform, and strongly dextro-rotatory.

A fine blue coloration is produced on adding a drop of strong sulphuric acid to a solution of sylvestrene in acetic anhydride.

TERPINOLENE. $C_{10}H_{16}$. (See also pages 259, 261.)

This terpene is produced together with terpinene by the polymerisation of other terpenes by sulphuric acid. It does not appear to exist in nature. In general characters it closely resembles dipentene. *Terpinolene tetrabromide* crystallises from ether in lustrous tablets which melt at 116°, and change on keeping to an opaque white mass, which begins to melt below 100°, evolving gas and yielding a green liquid.

TERPINENE. $C_{10}H_{16}$. (See also pages 259 and 261.)

Terpinene exists comparatively rarely in nature,[2] but occurs as a frequent product of the action of acids on other terpenes and their derivatives. Thus it is formed by the action of sul-

[1] Swedish turpentine oil is obtained from the *tar* resulting from the dry distillation of the roots and stumps of pines, whereas American turpentine oil is made from the resinous exudation of the same species of pine. This difference in origin may account for the absence of sylvestrene from the American oil. Sylvestrene is also present in various other pine oils.

[2] Terpinene has been found in Ceylon oil of cardamoms (*Elettaria cardamomum*).

phuric acid on pinene, phellandrene, dipentene, dipentene-glycol, and cineol.

For the preparation of terpinene, two litres of rectified oil of turpentine should be treated with 70 cc. of strong sulphuric acid. The acid must be added gradually, in quantities of 5 cc. at a time, so that the temperature may not rise above the point at which the flask can be conveniently handled. The mixture is agitated at frequent intervals for six or eight hours and the product then neutralised by caustic soda, and distilled in a current of steam. The distillate is fractionated, and the portion distilling at about 180° C., which consists of terpinene, collected separately.

Terpinene is a mobile liquid having an odour like that of lemons. It readily undergoes oxidation with formation of a resinous product.

Terpinene forms compounds with bromine and the halogen acids which are liquid at the ordinary temperature. The hydrochloride solidifies when strongly cooled.

Terpinene Nitrosite, $C_{10}H_{16}N_2O_3$, is obtained by the action of sodium nitrite and dilute acetic acid on terpinene. It crystallises from alcohol in white prisms which dissolve without change in strong acids, but are decomposed by boiling with an alkali. By adding ammonia to a hot alcoholic solution of the nitrosite, *terpinene nitrolamine* is obtained. This compound has probably the constitution $C_{10}H_{15}(O.NO)$: N.OH. It is deposited from its hot aqueous solution in needles, which melt at 116° to 118°, and dissolves easily in alcohol and alkalies. From the ethereal solution of the nitrolamine, hydrochloric acid precipitates crystals containing $C_{10}H_{18}N_2O,HCl$.

Other amines act with terpinene nitrosite in a manner similar to ammonia, forming crystallisable nitrolamines.

PHELLANDRENE. $C_{10}H_{16}$. (See also pages 259 and 261.)

Phellandrene exists in two optical modifications. The hydrocarbon from the oil of the water drop-wort (*Phellandrium aquaticum*) and many other plants is dextro-rotatory ($[a]_D = +17.6°$), but that from *Eucalyptus amygdalina* is lævo-rotatory. Wallach has produced evidence to show that the dextro-modification of the terpene found in oils of elemi and bitter fennel is not identical with the dextro-phellandrene found in water-fennel oil. These two phellandrenes are termed by Wallach α and β phellandrenes. The lævo-modification found in eucalyptus oils is lævo-α-phellandrene (*Annalen*, 1904, p. 9).

Phellandrene has not been so well studied as most other terpenes, and its compounds with the halogens and halogen acids are not very characteristic. The bromide is a heavy oil,

which is converted into cinene by heating with acetic acid and sodium acetate. By the action of hot alcoholic sulphuric acid, phellandrene is largely converted into terpinene. Phellandrene is one of the most easily altered of the terpenes. It is radically changed by contact with acids.

Phellandrene Nitroso-nitrite, $C_{10}H_{16}(NO)NO_2$, is the most characteristic and best-defined derivative of phellandrene. It does not appear to be formed by the action of nitrogen dioxide on phellandrene in the absence of air, but may be readily obtained by agitating the hydrocarbon with sodium nitrite and dilute acetic acid. Wallach describes the following process for its preparation: Phellandrene is diluted with petroleum and treated with dilute sulphuric acid in a beaker surrounded with a freezing mixture. A solution of sodium nitrite is then run in gradually, care being taken not to allow the temperature to rise above 4° C. Phellandrene nitroso-nitrite forms long needles which melt at 105° (Wallach).[1] Two physical isomerides exist, that from dextro-phellandrene being lævo-rotatory, while the isomer from lævo-phellandrene exhibits dextro-rotation. An optically-inactive modification is obtained by mixing the two active varieties in equal proportions.

From the fact that phellandrene nitroso-nitrite when dissolved in chloroform does not decolorise bromine, it appears to be a saturated compound. It differs from the corresponding derivative of terpinene in not yielding a nitrol-base on treatment with amines.

(On pseudo-phellandrene, see F. W. Semmler, *Ber.*, 1903, xxxvi, page 1749.)

THUJENE. $C_{10}H_{16}$.

This terpene is not known to occur in nature, but may be obtained by the dry distillation of the hydrochloride of thujylamine, a base prepared from thujene, one of the constituents of oil of thuja. Thujene has a specific gravity of about 0.838, and boils at 170 to 172°. Its molecule appears to contain two ethylenic bonds.

Thujene is distinguished from other terpenes by yielding an intense red coloration when its solution in acetic anhydride is treated with a drop of sulphuric acid.

Sesquiterpenes. Tripentines. $C_{15}H_{24} = (C_5H_8)_3$.

The hydrocarbons of this formula,[2] formerly called *cedrenes*, are closely allied to the true terpenes, and have often been

[1] According to O. Schreiner, phellandrene nitrosite melts, after repeated recrystallisation from hot alcohol, at 120° to 121° C.

[2] It has been suggested by W. A. Tilden that the sesquiterpenes possibly contain $C_{15}H_{26}$ instead of $C_{15}H_{24}$, and hence are homologous with the terpenes.

confounded with them. *They differ, however, from the terpenes* in the following important respects: They are viscous, instead of being limpid; have a comparatively high specific gravity (0.900 to 0.935 at 20° C.); boil at a high temperature (258° to 275° C.); form no crystalline hydrate similar to terpin (except caryophyllene); do not react with Riban's test; are not distinctly polymerised by sulphuric acid; and do not yield hydrogen peroxide by treatment with air and warm water.

When the sesquiterpenes are treated with bromine or iodine and the product distilled with water, *cymene* is produced, just as when terpeues are similarly treated.

The essential oils of allspice, ginger, cedar-wood, cubebs, hops, rosewood, calamus, Indian hemp, cascarilla, and patchouli consist chiefly or largely of sesquiterpenes. Oil of cloves rarely contains more than 20 per cent. of sesquiterpene, and often not more than 10 per cent.

A considerable number of sesquiterpenes have been described, but the distinct individuality of the great majority is highly questionable. The following are the best defined members of the class:—

Sesquiterpene.	Chief Sources.	Specific Gravity.	Boiling Point, ° C.	[a]D.	Other Characters.
Cadinene, ...	Oils of cade, galbanum, patchouli, &c.	0.918 at 20°	274 to 275	—98.6	S.$(HCl)_2$, m. p. 117° [a]D = —36.8°. S.$(HBr)_2$, m. p. 124° [a]D = —36.1°. S.$(HI)_2$, m. p. 105° [a]D = —48°.
Caryophyllene,	Oils of clove, copaiba, &c.	0.908 at 15°	258 to 260	lævorotatory	S.NOCl, white powder. S.N_2O_4, needles. Forms a crystalline alcohol melting at 96°. Refractive-index, 1.50094.
Clovene, ...	Isomerisation of caryophyllene.	0.930 at 18°	261 to 263	...	Does not form a crystalline alcohol. Refractive index, 1.50066.
Cedrene, ...	Oil of cedar-wood.	0.936 at 15°	262 to 263	—60	According to Rousset [a]D = —47.9°.
Humulene, ...	Oil of hops.	0.900 at 20°	263 to 266	...	Forms liquid S.Br_4 and S.$(HCl)_2$.S.NOCl crystalline.
Patchoulene, .	Action of dehydrating agents on patchouli alcohol.	0.939 at 23°	254 to 256	...	Refractive-index, 1.50094.
Zingiberene, ..	Oil of ginger.	0.872 at 15°	269 to 270	—69 to —73.5	Refractive-index, 1.49399. S.$(HCl)_2$, m.p. 168° to 169°; white needles. S.NOCl, white powder, m. p. 96 to 97°, with decomposition. Forms liquid S.Br_4.

In addition to the above, cubeb oil and betel-leaf oil contain the sesquiterpene *cubebene*, having a specific gravity of 0.917 at 15° and boiling at 260° C. Cubeb oil is said to contain a second sesquiterpene with a slightly different boiling-point, and pure cubebene is not improbably identical with cadinene.

The sesquiterpene of oil of patchouli (cadinene) is peculiar in forming an insoluble dihydrochloride, $C_{15}H_{24}$,2HCl, which is obtained when the fraction of the oii boiling between 260° and 280° is diluted with twice its volume of ether, and dry hydrochloric acid gas passed through it. The compound is separated by filtration, washed with alcohol, and recrystallised from ethyl acetate. The sesquiterpene is then regenerated by treating the hydrochloride with aniline and distilling the product in a current of steam. *Cadinene*[1] dissolves with difficulty in alcohol or glacial acetic acid, but is readily soluble in ether. It resinifies on exposure to air, and the partially oxidised substance, when dissolved in glacial acetic acid and treated with a few drops of strong sulphuric acid, is coloured first green and then indigo-blue, the colour changing to red on warming the mixture.

Caryophyllene and humulene present somewhat close resemblances in their physical properties, but the melting-points of their derivatives are very different. The following data have been recorded by E. Kremers (*Archiv. Pharm.*, 1898, i, 211):—

	CARYOPHYLLENE.[2]	HUMULENE.
Specific gravity at 20° C.,	0.9032	0.8977
Index of Refraction $[n]_D$,	1.50019	1.50094
Specific Rotatory Power $[a]_D$,	—8.74	—0.5
Melting Points of derivatives:—	° C.	
Nitrosochloride,	158 to 160	164 to 165
Nitrosate,	147 to 150	162 to 163
Nitrosite,	107	120 to 121
Isonitrosite,	53 to 56	165 to 168
Nitrol-benzylamine,	125 to 128	136
Nitrol-piperidine,	141 to 142	153

When boiled with alcoholic potash, the nitrosate of caryophyllene is converted into a compound which is apparently an *oxime*, crystallises in needles, and melts at 220° to 223°.

The sesquiterpene from the oil of Indian Hemp (*Cannabis Indica*) appears to be a distinct chemical individual, as shown by the results of various observers. E. J. Parry has suggested

[1] Patchoulene is not identical with cadinene. The former is an artificial sesquiterpene, prepared by dehydrating the natural *patchouli-camphor*.

[2] According to O. Wallach, the purest caryophyllene prepared from clove oil is optically inactive, boils at 259°, has a refractive index of 1.50009, and a specific gravity of 0.9085 at 15° C. The compounds with the halogen acids are liquid. S,NOCl melts at 162°; and S,N_2O_4 forms needles melting at 148°. A crystalline alcohol was obtained, which formed needles readily subliming, melting at 95° and boiling at 288°.

the name *cannibene* for this body, which was the name originally applied by Personne to a part of the oil of Indian Hemp which was not, however, a pure sesquiterpene.

CANNIBENE has been described as a mobile liquid boiling at 258° to 259° C., and having a specific gravity of 0.897 at 15°. It is lævo-rotatory, $[a]_D = -8.6°$.

Many other sesquiterpenes have been described by various observers, but the majority of them are probably mixtures largely composed of known sesquiterpenes.

Diterpenes and Polyterpenes.

These hydrocarbons are formed by the action of heat or polymerising agents on isoprene and the terpenes. They are not further polymerised by sulphuric acid, and combine with smaller proportions of hydrochloric acid than the unpolymerised terpenes. Their chemical characters have been little studied.

COLOPHENE, $C_{20}H_{32}$, or $(C_5H_8)_4$, is produced in considerable quantity when turpentine oil is agitated with strong sulphuric acid or phosphoric anhydride, and is present in rosin oil. It is a very viscid liquid of 0.939 specific gravity, which begins to boil at about 318°, and exhibits a strong blue fluorescence. It forms an unstable hydrochloride. Antimony trichloride converts turpentine oil into a colophene from which absolute alcohol extracts a liquid, leaving solid *tetraterebenthene*, $C_{40}H_{64}$, as an amorphous mass, soluble in ether, carbon disulphide, benzene, or turpentine, and melting above 100°. It is converted into liquid colophene by distillation.

The oils of black pepper, copaiba, and gurjun balsam contain a diterpene, or mixture of that nature, boiling at 250° to 260° C. The compound has not been obtained in a state of purity.

DITERPILENE, isomeric with colophene, is produced when oil of turpentine is heated with absolute formic acid. It is a thick oily liquid, optically inactive and smelling like copaiba balsam. It has a specific gravity of 0.9404 at 0° C., and resinifies on exposure to air.

POLYPRENE, $(C_5H_8)_n$, is the chief constituent of caoutchouc and guttapercha, and a body which appears to be an isomer exists in balata. From its specific refraction, Gladstone and Hibbert conclude that the group $C_{10}H_{16}$, as existing in polyprene, contains three double linkings and is an open-chain compound. Polyprene is very difficult to obtain in a state of purity, as it readily oxidises on exposure to air and light with formation of resinous bodies which occur with it in caoutchouc; but by repeated purifications a product containing only a very small proportion of oxygen is obtainable from rubber. Tilden obtained

pure polyprene by polymerising *isoprene*, C_5H_8 (prepared from turpentine oil), by treatment with concentrated hydrochloric acid.

Caoutchouc and Guttapercha.

(Appendix to Section on Polyterpenes.)

Caoutchouc. India Rubber.

Caoutchouc is a product obtained from the latex of trees growing in South America, Africa, India, &c.[1] It is obtained by tapping the trees by incisions which should be horizontal. From the latex obtained the rubber can be separated by churning at a temperature of about 50° C.

CAOUTCHOUC MILK OR LATEX is an opaque liquid, in appearance closely resembling animal milk. It appears under the microscope as an emulsion of globules about the size of the fat-globules of cows' milk floating in a "serum." The specific gravity of the latex is usually, but not invariably, below that of water; but when freed from caoutchouc the density of the serum varies from 1.037 to 1.040. C. O. Weber has stated (*Ber.*, 1903, xxxvi, 3108) that the caoutchouc does not exist as such in the latex, but is formed from the thin oily liquid, emulsified in the latex, by polymerisation. Other investigators, however, assert that the rubber exists ready-formed in the latex.

The following analyses of caoutchouc milk have been recorded by Girard and Lindet (*Analyst*, 1899, p. 78). The caoutchouc was determined by gradually adding an equal volume of 95 per cent. alcohol, with constant stirring, when the whole of the rubber collected on the surface, leaving an amber-colored liquid below:—

SOURCE OF LATEX.	SP. GRAVITY.	CAOUTCHOUC. (Per cent).
Pernambuco (*Hancornia*),	0.990	31.6
Africa,	0.987	33.4
Para (*Siphonia elastica*),	0.986	42.6
Nicaragua (*Castilloa elastica*),	0.980	32.3
Algiers (*Ficus macrophylla*),	1.000	37.5
" " "	1.005	37.1
" (*F. elastica*),	1.001	17.3
" (*F. nitida*),	0.971	31.3
" (*F. lævigata*),	1.005	28.0
New California (*Kickxia Africana*),	1.005	27.0

The crude caoutchouc of commerce is of very variable composition. It contains, besides the true rubber body, more or

[1] A new source of caoutchouc has been recently discovered in the root-bark of *Landolphia thrallonii*, a plant growing in Lower Guinea and the French Congo.

less resin, carbohydrates (including inosite), albuminous matters, colouring substances, ash-constituents and water. Accidental or added impurities, such as leaves, twigs, sand, clay, stones, colophony, &c., are often present.

The purification of crude caoutchouc is effected commercially by a process of maceration in water, which removes the soluble matters and a portion of the ash-constituents. For the purification of caoutchouc on a small scale it may be treated in succession with hot water, alcohol, and ether, the residue dissolved in chloroform, and the solution precipitated by alcohol.[1]

The chief constituent of caoutchouc is the hydrocarbon *polyprene*, $(C_5H_8)_n$ (page 278), a polymer of isoprene. Recent work by Harries points to the conclusion that the molecule of caoutchouc is probably a derivative of an eight-carbon cyclic compound (1 : 5 —dimethyl-*cyclo*-octadiene) and may have the following constitution:—

$$\left\{ \begin{array}{l} CH_3.C.CH_2.CH_2.CH \\ \quad\;\, \| \qquad\qquad\;\; \| \\ \quad CH.CH_2.CH_2.C.CH_3 \end{array} \right\} X.$$

Polyprene is difficult to obtain pure, as it absorbs oxygen and becomes brittle on exposure to light, with formation of a resinoid body of acid character ("Spiller's resin") stated to have the composition $C_{30}H_{48}O_{10}$, in which the ratio of C:H is the same as in polyprene. In addition to this oxidation-product, commercial rubber contains from 3 to 6 per cent. of a body which remains on treating the substance with the usual solvents, and, according to Weber, has the composition $C_{30}H_{68}O_{10}$.[2] The proportion in which it is present in rubber is

[1] Nees v. Esenbeck and Marquart allow the latex from *Ficus religiosa* to run into ether, mix the syrup obtained with more ether, and evaporate the decanted liquid. A colourless, elastic mass of caoutchouc is thus obtained, which is freed from admixed resin by boiling with alcohol.

C. O. Weber recommends that rubber be obtained free from mechanical impurities and albuminous matter by adding about 1 ounce of 40 per cent. formaldehyde solution to every gallon of strained diluted latex. After stirring and allowing to stand for one hour, a solution of sodium sulphate (1 lb. to a pint of boiling water, per gallon of latex) is added, which causes the rubber substance to rise in rapidly coalescing globules.

[2] This compound, the formula of which corresponds to $3C_{10}H_{16} + 10H_2O$ does not appear to be a product of the oxidation of polyprene. It seems to be closely allied to Spiller's resin, and Weber considers it to have an important relationship to the carbohydrates (inosite and its derivatives) found in crude rubber, being possibly a link between these carbohydrates (the celluloses especially) and the raw material from which the plant produces the hydrocarbons, including polyprene.

From the work of Harries and others, it is considered probable that the caoutchouc hydrocarbons have their origin in the breaking down of carbohydrates in the plant. Thus the penta-diënyl residues, C_5H_8, may result from the reduction of the pentoses, and may unite to form the complexes $(C_{10}H_{16})x$. (See *Chem. Soc. Ann. Reports*, 1905, pp. 80, 126, &c.)

probably too small to affect the quality of the latter. The proportion of oxygen in commercial caoutchouc is considered by Weber to afford a good criterion of the care with which the product has been collected, prepared and stored.

The resins from different brands of crude rubber vary greatly in their physical characters.[1] Many samples of rubber show an increased proportion of resin after vulcanisation, owing to the employment of too high a temperature or other improper treatment.

Caoutchouc is soft and elastic at ordinary temperatures, but below 0° it becomes hard and much less pliable. Newly-cut surfaces weld firmly together. Caoutchouc softens in boiling water, or when masticated for some time. Ordinary caoutchouc begins to melt at about 120° C.,[2] and remains soft and adhesive after cooling, but becomes hard again when spread out in thin layers. On heating it to 200°, it changes to a slimy mass which does not become hard on cooling. On dry distillation, caoutchouc yields *isoprene*, C_5H_8 (page 254); *dipentene* or *caoutchene*, $C_{10}H_{16}$ (page 270), and *heveene*, $C_{15}H_{24}$ or $C_{20}H_{32}$, which is a faint-smelling sharp-tasting liquid, boiling at 315° C.

Caoutchouc has a faint but characteristic odour. It is somewhat hygroscopic, but insoluble in water. It dissolves in ether, chloroform, benzene, toluene, petroleum-spirit, fused naphthalene, phenol, essential oils, and in carbon tetrachloride and disulphide. Its solubility in the last-named menstruum is much increased by the addition of absolute alcohol (8 per cent.). Masticated rubber dissolves much more readily than the crude product. Caoutchouc is a non-conductor of electricity, and becomes strongly electrified when rubbed.

Highly-purified rubber has a specific gravity of 0.911 at 17° C., and the technically pure substance from 0.915 to 0.931.

On exposure to air and light, rubber is oxidised to a hard resin somewhat resembling shellac. Hence articles of caoutchouc should be preserved in the dark in well-closed vessels. If they

[1] PONTIANAC, or "*dead Borneo*," is described by C. O. Weber as a resinoid substance usually occurring in the form of greyish-white cakes or balls. It loses 18 to 20 per cent. by washing with hot water, and can then be rolled into sheets. Pontianac becomes sticky even at a moderate temperature, and is used as an agglutinant for mixing with caoutchouc and mineral matters.

About 80 per cent. of pontianac is soluble in acetone. The soluble portion consists of a comparatively insoluble alban-like body, $C_9H_{12}O$, and of a yellow sticky substance, $C_4H_{10}O$, which, when dissolved in cold acetone and the solvent evaporated, forms a greyish mass having all the properties of an inferior caoutchouc. The portion of pontianac insoluble in acetone has the composition $C_{20}H_{32}O_5$.

[2] Gladstone and Hibbert state that purified caoutchouc does not melt even at 200° in the absence of air, and that its solution in toluene retains its optical properties at that temperature.

become hard, their elasticity may be restored by exposing them to the vapour of carbon disulphide, and subsequently of petroleum. Caoutchouc loses its elasticity and toughness when allowed to remain in contact with fatty oils, and certain metallic compounds, notably oxide of copper, bring about its rapid destruction.

Chlorine and bromine act energetically on caoutchouc to form both additive and substitution-compounds. Strong sulphuric acid chars and oxidises caoutchouc on heating, and nitric acid converts it into a substance of a yellow colour, which on prolonged boiling yields oxalic, camphoric, and camphoronic acids, with other products. Ozonised oxygen acts upon caoutchouc in chloroformic solution, producing a viscid oil, which finally sets to an explosive, glassy solid, of the composition $C_{10}H_{16}O_6$. Steam distillation of this ozonide yields lævulic aldehyde, and finally lævulic acid (Harries).

The yellow substance produced by the action of nitrous acid on Para rubber is said to have the composition $(C_{10}H_{15}N_3O_7)_2$. This compound melts at 160° C. with decomposition. It has acid properties, dissolves readily in alkalies, and is precipitated unchanged by acids (C. D. Harries, *Ber.*, 1901, p. 1123; 1902, p. 4429).

According to C. O. Weber (*Chemistry of India-rubber*), when *dry* nitrogen trioxide is passed into a solution of caoutchouc in benzene, *polyprene nitrosate*, $C_{10}H_{16}N_2O_3$, is formed. When nitrogen tetroxide (peroxide) is substituted, a body of the formula $C_{10}H_{16}N_2O_4$ is obtained. This compound is readily soluble in acetone, but almost insoluble in methyl and ethyl alcohols, ether, chloroform, and carbon disulphide. Rubber from various sources, guttapercha, and balata, after previous purification with acetone, all yielded an amount of this compound within one per cent. of the theory (167.6 per cent.). Hence the reaction has been utilised by Weber for the direct determination of real caoutchouc in raw and vulcanised rubber. (See page 309.)

The action of the halogens, oxides of nitrogen and vulcanisation agents, and the products obtained are fully discussed in an able paper by W. A. Caspari, who controverts some of Weber's statements and views (*J. S. C. I.*, 1905, p. 1274).

If to a hot solution (60° C.) of not more than 5 grammes of washed rubber in 300 c.c. of chloroform, alcohol be added drop by drop with constant stirring, the liquid becomes turbid, and finally a copious precipitation takes place. This fraction has been named α-caoutchouc by Schneider. The α-caoutchouc is filtered through silk-gauze, and separated from the filter, dried in hydrogen and weighed. More alcohol is added to the filtrate, when after the addition of a considerable amount of the alcohol, a further precipitation of rubber substance, β-caoutchouc, takes

place. This precipitate is treated as before. The residue from the evaporated filtrate is extracted repeatedly with boiling absolute alcohol, the insoluble matter being weighed as γ-caoutchouc. The three substances have the same empirical formula, $C_{10}H_{16}$, but they differ widely in their physical properties. The first fraction yields a firm and strong rubber, the second is considerably less firm, and is sticky, while the third fraction is still poorer in quality. The method has been suggested as likely to be of use in the valuation of rubber, but it should be used with caution in the case of unknown products, since oxygen-containing rubber gives abnormal results. (See *J. S. C. I.*, 1904, p. 328).

The following analyses have been placed on record by D. Morris (1903):—

	Rubber from British Guiana. (Per cent.)	Rubber from Dominica. (Per cent.)
Loss in washing,	17.00	8.22
α-Caoutchouc,	83.00	80.14
β-Caoutchouc,	0.00	0.00
γ-Caoutchouc,	10.34	3.19
Proteid,	1.14	4.44
Resins,	2.72	10.15
Ash,	1.82	1.58

Vulcanised Caoutchouc.

By treatment with sulphur or certain sulphur compounds, caoutchouc undergoes a remarkable change in properties. The product, known as "vulcanised rubber," is manufactured on an enormous scale. In some cases India-rubber cuttings are mixed intimately with from 7 to 10 per cent. of sulphur, and heated to a temperature ranging from 125° to 150° C. According to C. O. Weber, the vulcanisation of caoutchouc is due to the formation of a continuous series of *polyprene sulphides.*[1] The degree of vulcanisation obtained is dependent on the temperature and time allowed for the process and on the proportion of sulphur employed.[2] With pure caoutchouc there is no formation of hydrogen sulphide, but the insoluble oxygenated constituent of india-rubber ($C_{30}H_{68}O_{10}$) slowly combines with sulphur to form a substitution-product, sulphuretted hydrogen being evolved.

[1] According to C. A. Burghardt, probably not more than 2.5 per cent. of sulphur exists in actual combination in vulcanised caoutchouc. By prolonged aërial exposure, the excess of sulphur decreases, apparently by a process of oxidation. Burghardt holds that the amouut of oxygen taken up or combined with the caoutchouc is an index of the amount of deterioration which it has undergone.

[2] The chemical changes which occur in the vulcanisation of caoutchouc are very imperfectly understood, though they have been the subject of various researches and of heated controversies (see C. O. Weber, H. L. Terry, W. Thomson, &c., *J. S. C. I.*, xiii (1894), pp. 11, 473, 987; xiv (1895), pp. 436, 758, 1051; xviii (1899), p. 1034; xxi (1902), p. 712).

Sulphur "carriers" are largely employed for accelerating and facilitating vulcanisation. Those chiefly employed are antimony and arsenic pentasulphides, orpiment and realgar. Less active carriers are the sulphide of zinc, and the oxide, carbonate, sulphide and thiosulphate of lead. Vulcanisation by means of metallic iodides (*e. g.*, antimony iodide) has also been employed.

In Parkes' cold process, the articles to be vulcanised are immersed in a solution of 2.5 parts of sulphur chloride[1] (S_2Cl_2) in 100 of carbon disulphide, or in the case of waterproof fabrics, the material is sponged over with the solution. The reaction in Parkes' process is held by C. A. Burghardt to consist in the substitution of sulphur for a portion of the hydrogen of the caoutchouc, hydrochloric acid being simultaneously formed. Caoutchouc vulcanised by Parkes' process always contains a notable quantity of chlorine as well as sulphur, and, according to Weber, a series of chlorosulphides of polyprene are formed.

In the process of Gerard, the caoutchouc is soaked for some hours in a solution of potassium pentasulphide (sp. gr. 1.25) heated to 140°, and then washed and dried.

Vulcanised caoutchouc is greyish in colour and not adhesive. It remains elastic and pliable in the cold. Unlike raw rubber, vulcanised caoutchouc does not absorb any appreciable quantity of water, and only swells up, without dissolving, in the ordinary solvents of caoutchouc. It slowly absorbs atmospheric oxygen, and in an atmosphere of carbon dioxide takes up about its own volume of the gas. Vulcanised rubber usually contains a portion of its sulphur as a mechanical mixture, and this is extractable by boiling the substance with caustic soda, a treatment which prevents the rubber from becoming hard and brittle.

EBONITE. VULCANITE. When the proportion of sulphur employed in vulcanising rubber is very large (*e. g.*, 30 per cent.) and the articles are heated to 150°, a plastic mass is obtained which on cooling possesses the consistency of horn, and can be turned and worked in the same way. The product forms the vulcanite and ebonite of commerce.[2]

Ebonite and similar hard rubber products frequently contain

[1] The purity of the sulphur chloride employed for the vulcanisation of rubber greatly affects the quality of the vulcanised rubber obtained. Samples of sulphur monochloride containing sulphur dichloride, SCl_2, should not be employed, since this compound causes over-chlorination of the rubber. The presence of much free sulphur in sulphur chloride used for vulcanisation causes efflorescence of sulphur on the surface of the rubber, but this is not objectionable except in appearance. The best sulphur chloride for vulcanisation purposes is that which most nearly approximates to the composition S_2Cl_2.

[2] *Balenite* is a product, intermediate between soft rubber and ebonite, obtained by heating a mixture of ten parts of caoutchouc with two parts of shellac, calcined magnesia, sulphur and antimony sulphide.

certain resins (such as shellac and colophony), asphalt and pitch, and other substances in admixture. According to Heinzerling and Pahl (*J. S. C. I.*, 1892, p. 536), the quality of hard rubber is much deteriorated by the addition of rosin oil and resin, while on the other hand asphalt increases the strength and elasticity of the product.

Guttapercha.

Guttapercha occurs in the *latex* of various trees belonging to the *Sapotaceæ* (e. g., *Palaquium pustulata* and other species), growing in the Malay peninsula and archipelago. It is called "*percha*" by the natives, "gutta" being the Malay name for gum.

The extraction and purification of guttapercha have been fully described by E. F. A. Obach.[1] (See Cantor Lectures, *Jour. Soc. Arts*, 1897 and 1898; abst. *J. S. C. I.*, 1898, p. 470).

The crude guttapercha of commerce is a reddish, marbled mass, which often contains sand, pieces of wood, portions of bark, &c. It is said that a plastic gum, probably *balata*, is sent from London to Singapore to be mixed with the guttapercha. The commercial product is certainly very frequently and largely adulterated. Guttapercha is purified by thoroughly washing the fine shavings with cold and hot water, and then kneading them into blocks. The product obtained by extracting the leaves, twigs, &c., of the guttapercha tree is much purer than the ordinary commercial guttapercha.[2]

Guttapercha dissolves in all the solvents of india-rubber. It is hard, tough, and slightly elastic at the ordinary temperature, becomes pliable at 25°, and gradually softens on heating. When pure it has a specific gravity of about 0.961. At 60° it is so plastic that it may be pressed into any shape or drawn into threads. It becomes adhesive at 100°. When boiled in water, it swells up somewhat and takes up about 5 to 6 per cent. of water, but loses this gradually on subsequent exposure to air. When exposed to air and sunlight, guttapercha absorbs oxygen like caoutchouc, and becomes brittle. Guttapercha is also quickly acted upon by ozone. It can be preserved in the dark or under water, especially sea-water, without undergoing any

[1] According to *Brit. Patent*, 1896, No. 19046, the crushed stems, leaves and twigs are extracted with light petroleum. Melted paraffin-wax may also be used for the extraction. W. Ramsay (*Brit. Patent*, 1897, No. 17936) substitutes rosin oil for the toluene usually employed (*Brit. Patent*, 1896, No. 654).

[2] On a small scale, guttapercha may be obtained pure and colourless by treating it with boiling alcohol, dissolving the residue in chloroform or hot benzene, decolourising the solution with animal charcoal, and then precipitating with alcohol.

alteration. It is not attacked by alkalies or hydrofluoric acid, which is therefore commonly stored in bottles made of this substance. Guttapercha is a non-conductor of electricity.

Unlike caoutchouc, guttapercha has a cellular structure, which becomes fibrous when subjected to tension. It is very porous, and hence many specimens float on water.

The action of nitrous acid gas (N_2O_3) upon guttapercha is similar to its action upon rubber, the nitrosite, $C_{10}H_{15}N_3O_7$ (Harries' "nitrosite C."), being apparently formed. Balata also gives a nitrosite closely resembling "nitrosite C." in its chemical characters. (See a paper by W. A. Caspari, *J. S. C. I.*, 1905, p. 1274).

By mixing it with sulphur and heating, guttapercha may be vulcanised like caoutchouc, and with a larger proportion of sulphur it yields a body resembling ebonite. According to Macintosh, a similar body is obtained by treating guttapercha with concentrated sulphuric acid. Guttapercha is often mixed with caoutchouc in various proportions to increase its elasticity.

Guttapercha is largely employed for the insulation of wire and for the construction of electric cables. Bleached guttapercha is used as a filling and setting for teeth. It is employed for surgical purposes in the form of guttapercha tissue. A solution of guttapercha in chloroform, known as "*traumaticin*," is used as a substitute for collodion.

The composition of guttapercha is exceedingly complex, and the existing knowledge of its chemistry is very imperfect. Payen in 1851 found guttapercha to contain *gutta*, *alban*, and *fluavil*. More recently H. Bornträger (*Zeit. anal. Chem.*, 1900, page 502) found alban to consist of several distinct bodies. The "albans" and "fluavils" are oxidation-products of gutta.

"GUTTA" has the empirical formula C_5H_8, but is probably a mixture of several polymers of this ultimate composition. (Compare polyprene, page 280.) On dry distillation gutta yields *isoprene*, C_5H_8, and two hydrocarbons of higher boiling-point, probably containing $C_{10}H_{16}$ and $C_{30}H_{48}$. According to Ramsay, Chick and Collingridge (*J. S. C. I.*, 1902, p. 1367), no compound of the formula $C_{10}H_{16}O$ is obtainable by the direct action of chromic acid on gutta, though such a body results, with others, from the treatment of alban with oxidising agents.

Gutta forms from 40 to 85 per cent. of commercial guttapercha. At ordinary temperatures it is white and soft but not elastic, while at 45° C. it becomes yellow and pasty, and at 100° to 110° softens, melting and boiling at 130° with decomposition. Gutta is soluble in chloroform, toluene, and carbon disulphide, but insoluble in absolute alcohol, or in ether after treatment with alcohol. Gutta oxidises in the air, and hot nitric acid decomposes it with production of formic acid and other products.

"ALBAN" is described as a mixture of white resins, soluble in hot alcohol. A crystalline body containing $C_{17}H_{28}O$ and a resinous substance of the formula $C_{17}H_{28}O$ have been recognised, and a third constituent is also stated to be present (see also A. Tschirch, *Arch. der Pharm.*, ccxli, 481; abst. *J. S. C. I.*, 1903, p. 1250).

"FLUAVIL," $C_{40}H_{64}O_3$(?), is a yellow amorphous resin, softening at about 50° and boiling at 105°. It dissolves in cold alcohol, in which the alban resins are practically insoluble.

Recent work by Tschirch and Müller (*Archiv der Pharm.*, ccxliii, 114) goes to show that the three "albans" of the guttapercha from New Guinea are distinct from those of the Sumatra product, while "fluavil" is apparently a mixture of two bodies of different melting points. Tschirch describes the albans as bodies soluble in boiling alcohol, fluavils soluble in cold alcohol, and the "albanans" as substances insoluble in both hot and cold spirit. Caoutchouc is stated to contain alban-like substances.

The following figures, showing the composition of commercial guttapercha and balata, are given by E. F. A. Obach (*Jour. Soc. Arts*, 1897 and 1898; abst. *J. S. C. I.*, 1898, page 470)[1]:—

DESCRIPTION OF MATERIAL.	PERCENTAGE COMPOSITION.			
	Gutta.	Resin.	Dirt.	Water.
RAW GUTTAPERCHA.				
Range,	23.1 to 84.3	10.1 to 65.2	1.8 to 22.3	1.0 to 26.7
CLEANED GUTTAPERCHA.				
Range,	24.4 to 88.8	11.2 to 67.4	0.9 to 2.0	0.5 to 2.3
Sample A,	78.1	19.2	1.5	1.2
B,	57.5	40.9	1.0	0.6
C,	52.2	45.4	1.5	0.9
D,	55.6	40.9	1.8	1.7
HARDENED GUTTAPERCHA.				
Medium quality, cleaned only,	54.7	39.4	2.7	3.2
Same sample after hardening,	93.0	2.8	2.5	1.7
BALATA.				
Raw; average,	43.0	39.6	10.0	7.4
Cleaned; average,	52.1	47.9	...	...

The following figures show in more detail the approximate range of composition of commercial guttapercha, according to the results of various observers:—Water, 1.0 to 1.5 per cent.; dirt (woody-fibre and soil) 3 to 5; pure gutta, 30.5 to 83.5; "alban," 7.0 to 44.5; and "fluavil," 3.0 to 21.0 per cent. The ash of guttapercha rarely, if ever, exceeds 0.5 per cent.

[1] Other analyses of guttapercha from various botanical sources have been published by V. Romburgh and T. de Haas (*J. S. C. I.*, 1903, p. 752). See also *J. S. C. I.*, 1904, p. 552, for further figures.

W. G. Berry (*J. S. C. I.*, 1904, page 529) has published figures showing the acid and ester values of guttapercha and allied substances.

The chief data for the valuation of guttapercha are to be found in the determination of the moisture, the amount of pure gutta, and the proportion of impurities, such as dirt, &c. The larger the proportion of gutta in a sample (and therefore the smaller the amount of resin), the more valuable it is for commercial purposes. For the insulation of telegraph cables an article containing not less than 65 per cent. of gutta is required. It is stated, however, by W. A. Caspari, that the resin of guttapercha is the insulating constituent, and that it is the aim of the insulated wiremaker to obtain a product containing this resin with sufficient gutta to give the desired mechanical properties.

BALATA is obtained from the latex of *Mimusops balata*, a tree growing in Guiana and Brazil. The commercial product forms a leathery mass, and contains oxygen. Balata has a specific gravity of 1.044 and melts at 149° C. It contains "alban" and "fluavil," and thus resembles guttapercha. The pure hydrocarbon separated from balata is isomeric with that from guttapercha and caoutchouc, which it closely resembles, and like the latter can be vulcanised. Balata is elastic like caoutchouc, and becomes plastic on heating (at 50° C.) like guttapercha. The composition of raw and cleaned balata is given on page 287.

Formerly, balata was employed for coating telegraph wires, surgical instruments, &c. It is now largely used, in the United States, for chewing-gum, fifty tons per annum being said to be consumed for this purpose. The production of balata has recently decreased, owing to the fact that the tree, which grows in very unhealthy districts, is no longer cultivated and is slowly dying out.

Analytical Examination of Caoutchouc, &c.

In the analysis of caoutchouc and guttapercha it is important to reduce the material to a fine state of division. This is best effected by a miniature macerating apparatus, such as is used in the commercial treatment of rubber, but in default of this the sample must be reduced by rasping or cut up fine by scissors. In consequence of the difficulty of obtaining the substance in a finely-divided state, processes in which the sample is dissolved in benzene or chloroform and the solution precipitated by acetone are preferable to those in which the material is treated direct with acetone or alcohol. The insolubility of vulcanised rubber in ordinary solvents renders this process inapplicable to its analysis. It is desirable that a fairly large quantity of the

rubber for analysis be sampled, owing to the lack of uniformity of many specimens.

ANALYSIS OF RAW CAOUTCHOUC AND GUTTAPERCHA.

For the valuation of crude india-rubber and guttapercha, C. O. Weber determines the loss on washing, the proportion of oily and resinous matters, the percentage of combined oxygen and the amount of mineral matters.

The *loss on washing*, which represents water, woody and other fibres, soluble salts and other mineral matters, is not an indication of the quality of the crude substance, but the amount of such loss influences the price of rubber in its manufactured condition. Para rubber was found by Weber to give a mean loss of about 16 per cent. on washing, other brands of rubber giving results ranging from 8 to 48 per cent.

The proportion of *oily and resinous matters* is ascertained by Weber by extracting 5 to 10 grammes of the washed rubber (dried *in vacuo* or in a current of carbon dioxide) with acetone for six to ten hours in a Soxhlet apparatus. The acetone is distilled, the resinous matter dried at 100°, and its weight calculated on the washed rubber. The presence of oily and resinous matters in rubber renders the latter softer and easier to work in manufacture, but they cause retardation of the vulcanisation process, and thus it is difficult to obtain uniformity in the manufactured product unless the proportion of these bodies remains fairly constant in the same brand. Fine Para contains only about 2 per cent. of resins, while most other varieties contain proportions ranging from 2 to about 14 per cent. The following figures have been recorded by H. L. Terry (*J. S. C. I.*, 1889, p. 218), C. O. Weber (*J. S. C. I.*, 1894, p. 477), and R. Henriques (1899):—

VARIETY OF RUBBER.	RESIN (PER CENT.)		
	Terry.	Weber.	Henriques.
Para, fine,	1.2	1.3	1.3
Mozambique,	3.0	3.2	3.8
Sierra Leone, red,	7.4	9.7	5.8
Assam,	9.3	11.3	11.3
African Ball,	22.8	26.1	...
African Flake,	41.2	63.9	...

Henriques' figures were apparently obtained by extraction with acetone. Terry's results were obtained by extracting the finely-cut rubber for several hours in a Soxhlet tube with alcohol.

Weber considers this process too tedious, and prefers to dissolve 50 grammes of the dry rubber in one litre of benzene, filter through silk-gauze, and add 100 c.c. of the filtrate very slowly to 200 c.c. of alcohol. The true caoutchouc is precipitated, while the resin remaining in solution is determined by filtering the liquid, washing the precipitate with hot alcohol, and weighing the residue left on evaporating the filtrate.[1]

The foregoing processes of extraction by acetone or alcohol are apt to give results below the truth, since they ignore the presence of resinous bodies insoluble or but slightly soluble in these menstrua. This is notably the case with rubber from Sierra Leone, in the extraction of which glacial acetic acid should be employed.

The *oxygen* in rubber is determined by Weber by submitting a known weight of the washed sample (previously extracted by acetone and dried in a current of hydrogen or carbon dioxide) to a combustion process, thus ascertaining the amount of carbon and hydrogen in the rubber, and the amount of oxygen by difference. Any mineral matter left in the combustion-boat must be deducted from the weight of rubber taken for analysis. Weber found from 1.2 to 7.4 per cent. of oxygen in various brands of rubber (ash-free).

The *mineral matter* in crude rubber, as deduced from the ash left after combustion, is approximately correct for those brands of rubber containing not more than 4 per cent. of resinous bodies. Larger proportions of resins carry some of the mineral matter with them into the acetone extract. In such cases, the ash should be determined on the washed rubber which has not been extracted with acetone. The ash of various brands of washed extracted rubbers was found by Weber to range from 0.3 (in the case of fine Para) to 5.3 per cent.

For the analysis of *guttapercha*, Marckwald and Frank recommend (*Analyst*, 1903, xxviii, 13) that 2 grammes of the dried sample should be dissolved in 15 c.c. of chloroform, and the clear solution poured gradually, with constant stirring, into 75 c.c. of acetone. The *gutta* forms a voluminous porous cake, which can be pressed out, washed with acetone without loss, dried at 100° C., and weighed. The dirt and insoluble matters, if not previously separated, may be determined by passing the solution and washings through a tared filter. Any small particles of gutta separated by the filter may be dissolved in hot toluene and added to the main portion.

Alcohol cannot be substituted for acetone in the above process, but good results are obtainable by dissolving 2 grammes of gutta-

[1] By treating samples of pure Para rubber, finely-cut, with two successive quantities of boiling alcohol for six hours, the following percentages of resin were found by A. R. Tankard in the author's laboratory:—Raw Para rubber, 2.27; washed, 2.83; and vulcanised, 2.13 per cent.

percha in 10 c.c. of chloroform and adding 100 c.c. of ether. After standing for twenty-four hours, the precipitated gutta is filtered off.

H. Bornträger (*Zeit. anal. Chem.*, 1900, p. 502) boils one gramme of the sample of guttapercha for twelve hours under a reflux-condenser with 50 c.c. of benzene, filters from dirt, &c., and washes the residue with hot benzene. The filtrate and washings are then evaporated to 50 c.c., and mixed with two measures of absolute alcohol. After standing on the water-bath for some hours the *gutta* is completely precipitated, and is filtered off, washed three times with hot alcohol, dried at 100° and weighed. For the separation of the resins, the filtrate should be evaporated nearly to dryness, and the residue taken up with 50 c.c. of boiling absolute alcohol.[1] The solution is transferred to a weighed capsule or beaker, and allowed to stand in the cold for twenty-four hours. The liquid, containing the fluavil in solution, is decanted, and the residue of "*albans*," well washed with cold alcohol, dried at 80° C., and weighed. The "*fluavil*" can be recovered by evaporating the alcoholic solution, and drying the residue at 80°, but loss is liable to occur from volatilisation.

ANALYSIS OF UNVULCANISED CAOUTCHOUC MIXTURES.

For the determination of *unsaponifiable oils* in non-vulcanised products, R. Henriques (*Analyst*, xxiv, 1899, p. 297) treats the sample with hot acetone as long as the solvent is coloured. Owing to the solvent action of ether on non-vulcanised rubber, this liquid cannot be employed. Since the residual rubber is not easily dried, it is preferable to distil the acetone, redissolve the oils in ether, and filter the ethereal solution into a weighed flask. The ether is then distilled and the residue weighed.

Owing to physical difficulties, the ordinary alcoholic soda extraction-process for the determination of fatty substitutes (page 303) is not suitable for the analysis of sheets composed of soft rubber and substitutes, although it may be used in the examination of non-vulcanised "patent" rubber plates. Hence in the former case the process is modified by Henriques as follows:—A weight of 5 grammes of the sample is boiled under an inverted condenser with 25 c.c. of benzene for an hour, and allowed to rest over night. Twenty-five c.c. of normal alcoholic alkali are added, and the boiling is repeated for four hours. The solvents are removed on the water-bath, and the residue is rinsed into a large basin with hot water. It is extracted with boiling water several times, the alkaline liquor being poured away. The residual rubber is kneaded and boiled with water till no longer alkaline, and is finally dried at 100° C.

[1] This plan is preferable to that of Bornträger, who evaporates the mixed alcohol and benzene to 50 c.c., with the result of obtaining a residual liquid of uncertain composition.

Analysis of Vulcanised India-rubber.

The complete analysis of a complex india-rubber article by physical and chemical tests is rarely required and would be a very tedious operation. Only in the investigation of the causes of premature decay or unexpected breakdown of manufactured rubber, when physical tests are useless, is a complete analysis necessary.

As is well known, india-rubber goods are rarely manufactured from india-rubber only, and generally contain one or more of the following substances in admixture:—mineral matters, rubber substitutes or surrogates (oil substitutes), recovered rubber, bituminous substances (asphalt, &c.), resins, rosin oil, fatty oils, albumin, and paraffin-wax.

There are many difficulties to be overcome in the analysis of rubber articles. Substances added to the rubber before vulcanisation become changed on treatment with sulphur, and no longer exist in the same form, often becoming insoluble in their usual solvents. The analysis of rubber resolves itself into the recognition and determination of the substances originally mixed to make the finished article, a problem far more complex than that of the proximate analysis of the finished article.

The difficulty of obtaining a homogeneous sample of manufactured rubber is often considerable. Fairly large quantities of the substance should be taken, and this, by cutting, rasping, or other suitable means, brought into a very fiuely-divided condition.

The *specific gravity* of india-rubber is of little or no value in judging of its purity or quality. Samples which float on water are usually free from any notable admixture of mineral matters, but the test is not absolute, as manufactured rubber frequently contains air-vesicles. Rubber having little porosity is to be preferred for most purposes. Certain organic substances, such as tar-products, reduce the porosity of rubber, and hence are sometimes valuable.

The *apparent* specific gravity is observed by placing conveniently large pieces of the rubber in water, and, if the pieces float, adding alcohol, stirring the mixture well after each addition. If they sink, a concentrated solution of calcium chloride should be added, until the pieces remain suspended in the liquid, neither floating nor sinking. The specific gravity of the liquid is then determined.

The *real* specific gravity of rubber is determined by placing as much as practicable of the finely-divided sample in a specific gravity bottle with some distilled water, attaching the bottle to the air-pump and exhausting the rubber until free from occluded air. To obtain the rubber in a sufficiently fine state of division, a pair of laboratory mixing-rollers should be used, or the sample should be rasped. The latter method is quite successful provided the rubber contains an appreciable amount of mineral matter.

The porosity of a sample of rubber, expressed in whole numbers, is therefore:—

$$p. = \left\{ \frac{\text{real sp. gr.}}{\text{apparent sp. gr.}} - 1 \right\} 1000.$$

A non-porous rubber will of course give p. = 0. The porosity of a sample is influenced not only by the amount but also by the nature of the admixtures, the highest porosity being shown by samples containing considerable quantities of rubber substitutes and recovered rubber.

The *elongation* and *tensile strength* of rubber are useful mechanical tests, as are also the electrical tests of insulation and electrostatic capacity. These will be found fully described in Weber's *Chemistry of India-rubber.*

Many samples of rubber are liable to develop cracks due to oxidation, and this is known as "suncracking." To measure the tendency of rubber to suncrack, Weber mixes 20 grammes of acetone with 60 c.c. of a 20 per cent. solution of hydrogen peroxide, and allows the mixture to stand for a fortnight before being used. The solution will keep for a long time. Weighed strips of equal area of the sample to be tested and of the standard with which it is to be compared are immersed in this solution for at least two days, when the strips are withdrawn, washed with acetone, then with water, and dried at 100°. The increase in weight shows the amount of oxygen absorbed. The method is very suitable for the examination of tyre-covers.

The inorganic materials mixed with rubber during manufacture are used:—(1) for the purpose of "filling," that is, to produce a larger bulk, and so reduce the cost of the manufactured article; (2) as sulphur-carriers, which hasten the vulcanisation of the rubber or influence it in some way; or (3) to give the finished article a definite colour. Some of the sulphur-carriers are as much used for their "filling" properties and for their colouring value as for any influence they have on the vulcanisation. The compounding materials employed are usually practically insoluble in water, and chemically inert at temperatures ranging from 180° to 200° C.

Since red lead is a hardening agent in india-rubber and is used in admixture with the "soft" brands of rubber, the presence of this inorganic material is generally evidence of the low quality of the rubber in the sample. Barium and calcium hydroxides and magnesium oxide possess a remarkable hardening action upon rubber, and are frequently added in small quantities for this purpose.[1]

[1] Heinzerling and Pahl have recorded the results of an extensive research into the influence of various inorganic and organic admixtures in rubber (*J. S. C. I.*, 1892, page 536). Their results show that the quality of rubber is much improved for some purposes by the addition of certain mineral matters, while the specific gravity of the product may be modified by admixture with paraffin-wax or blown oil. Rubber vulcanised with ten per cent. of sulphur was found to be the most elastic. All mineral

The *ash* left on the ignition of rubber articles is not a true criterion of the amount of mineral matter in the original sample, the results being frequently 2 per cent. in excess of the truth. This is due to the reducing action of organic matters upon inorganic substances (as, for example, sulphates), and to the fact that part of the organic sulphur reacts with metallic oxides to form sulphides. Some compounds (such as those of arsenic, antimony, and mercury) volatilise more or less completely on ignition, and carbonates are more or less converted into oxides.

Notwithstanding these sources of error, a determination of the "ash" is of distinct value, provided the above considerations are borne in mind. The determination should be made by careful ignition of a thin layer of the finely-divided sample in a porcelain dish, employing as low a temperature as possible and regulating the heat so that the vapours given off do not inflame. The mineral matter thus obtained may then be subjected to the usual methods of analysis, but when information is desired as to the form in which the inorganic constituents exist in the rubber, it is better to isolate the mineral matter in other ways. (See pages 306, 309.)

For the determination of *mineral matter* in rubber goods, L. de Koningh (*Jour. Amer. Chem. Soc.*, xix, 1897, page 952) treats 5 grammes of the very finely-divided sample with 50 c.c. of hydrochloric acid (sp. gr., 1.16) and allows it to soak for one hour in the cold, afterwards heating the liquid to 70° for an hour. Fifty c.c. measure of water is then added and the insoluble matter washed with boiling water till free from acid reaction. The residue is then dried at 105°. The weight obtained, subtracted from that of the rubber taken, gives the greater part of the soluble mineral matters of the sample.[1] The insoluble mineral matter, which may contain barium sulphate and silicates, is obtained by ignition of the rubber residue. Barium sulphate is soluble in hot strong sulphuric acid, and may be completely re-precipitated from this solution by dilution with water.

According to C. A. Lobry de Bruyn (*J. S. C. I.*, 1894, page 986), the mineral matter of manufactured rubbers should consist

and organic substances diminished the elasticity of rubber goods, while the addition of oxides of zinc, lead, magnesium and calcium, calcium carbonate, pitch and glycerin, increased their strength. Organic admixtures such as paraffin-wax, rosin and pitch, and small quantities of oil substitutes increased the insulating-power of rubber, but the mixtures did not resist the action of high temperatures so well as pure rubber. Certain mineral matters, such as the oxides of zinc, calcium and magnesium (the last-named only in small quantities), and calcium carbonate also increased the insulating-capacity of rubber. Large quantities of magnesium oxide, however, and additions of vermilion and lead oxide, decreased the insulating power. Rubber containing certain organic admixtures (such as paraffin-wax, asphalt and oil-substitutes) was found to have an increased power of resisting the destructive action of oil.

[1] The acid used has a slight action upon the rubber, dissolving it to the extent of about one per cent.

of zinc-white only, except when the rubber (*e. g.*, laboratory corks and tubing, &c.) has to come into contact with acids; in such cases it should consist of barium or lead sulphate.[1] Red rubbers should be vulcanised with antimony sulphide and should not contain any ferric oxide. All other articles for laboratory use should be made from pure ash-free rubber.

The dry and moist heat tests for rubber goods, known as the "British Admiralty Test," are valuable as showing what effect heating, or subjection to steam at high pressure, will have upon the sample. For the dry heat test, a small weighed portion of the sample is placed in an air-oven and kept at a temperature of 135° C. for two hours. The moist heat test is carried out by heating a small weighed piece of the rubber in a sealed tube half filled with water, or in a "digester," provided with a pressure-gauge and thermometer, for four hours at a temperature of 170° C. (or, according to Weber, for three hours at 320° F. = 160° C.). The general behaviour of the samples and the loss of weight are noted. The dry heat should not cause a loss of more than 1.5 per cent. in weight, and the sample should not have suffered by the moist heating.[2] Inferior rubbers and those containing substitutes are more or less damaged by the above tests, becoming hard and brittle and losing their elasticity, or swelling and fusing. R. Henriques does not place much reliance on these tests, and contends that the loss in weight depends on the amount of free sulphur present, and the volatilisation of this constituent by the heating. Increase of weight also takes place by oxidation, to some extent in ratio with the proportion of combined sulphur. Weber considers that although the Admiralty test may furnish indications as to the behaviour of a sample under working conditions, yet its indiscriminate application to all classes of rubber articles is likely to be mischievous and misleading when, as is frequently the case, it imposes upon rubber goods test-conditions bearing no relation to those under which the goods are to be used.

The following method of analysing complex rubber articles has been described by C. O. Weber (*Chemistry of India-rubber*). The scheme is a valuable adaptation of processes devised by Henriques, Weber, and others:—

[1] *Lithopone*, $ZnS + BaSO_4$ (with some ZnO), prepared by precipitating a solution of zinc sulphate by barium sulphide and roasting the mixture, is much used in the manufacture of drab rubber goods which are to be subjected to the action of alkalies. Lithopone is not suited for the manufacture of rubber goods which are to come into contact with acids.

[2] The loss of weight of many common rubbers containing surrogate may, however, be as small as in the case of genuine rubbers containing a moderate proportion of rubber-resin; but surrogate-containing rubbers do not stand the moist heat test, since they fuse and become decomposed. (L. de Bruyn and van Leent, *Chem. Zeit.*, xviii, 309, 329; abst. *J. S. C. I.*, 1894, page 963).

SCHEME OF RUBBER ANALYSIS.

<table>
<tr><td colspan="6">Two grammes of the sample is extracted with acetone (page 297).</td></tr>
<tr><td rowspan="5">(A) SOLUBLE IN ACETONE.

Resinous constituents of India-rubber.
Fatty Oils.
Mineral Oils.
Resin Oils.
Solid Hydrocarbons.
Resins.
Free Sulphur.</td><td colspan="5">(B) RESIDUE. Extracted with Pyridine.</td></tr>
<tr><td rowspan="4">(C) SOLUBLE IN PYRIDINE.

Tar. Pitch.
Bituminous bodies.
Sulphur in above.</td><td colspan="4">(D) RESIDUE. Extracted with Alcoholic Potash.</td></tr>
<tr><td rowspan="3">(E) SOLUBLE IN ALCOHOLIC POTASH.

Chlorosulphide substitutes.
Sulphide substitutes.
Oxidised (Blown) Oils.
Sulphur in substitutes.
Chlorine in substitutes.</td><td colspan="3">(F) RESIDUE. Extracted with Nitro-naphthalene.</td></tr>
<tr><td rowspan="2">(G) SOLUBLE IN NITRO-NAPHTHALENE.

India-rubber.
Sulphur in India-rubber.
Chlorine in India-rubber.
(The total of the above three constituents is determined by loss.)</td><td colspan="2">(H) RESIDUE. Extracted with Boiling Water.</td></tr>
<tr><td>(I) SOLUBLE IN BOILING WATER.

Starch.

Dextrin.</td><td>(K) RESIDUE.

Mineral Matter.
Free Carbon.
Fibrous materials.
Sulphur in inorganic compounds.</td></tr>
</table>

Separate determinations should also be made of the total sulphur and chlorine in the sample (pages 313, 314).

The foregoing scheme of analysis is so comprehensive as to include practically every likely constituent present in any class of manufactured rubber. Hence it is rarely necessary to go through the whole scheme with any one sample, and the process may be much shortened in most cases. This is true of samples the mineral matter of which contains neither sulphides, sulphates, nor any other compounds of sulphur, and the detailed composition of which is not of first importance. Also if the sample is of the "grey" or "red" variety, the process may be further curtailed by the omission of the pyridine extraction, since these varieties never contain tar, pitch or bituminous matters. The method of procedure in such cases is then as follows[1]:—

Two grammes of the sample is extracted with acetone (see below).		
SOLUBLE IN ACETONE.	RESIDUE. Extracted with Alcoholic Potash.	
	SOLUBLE IN ALCOHOLIC POTASH.	RESIDUE. (Rubber-matter, &c.)
(See previous table on page 296.)	Chlorosulphide Substitutes. Sulphide Substitutes. Oxidised (blown) Oils. Sulphur in substitutes. Chlorine in substitutes.	Sulphur in rubber (= S. of vulcanisation). Chlorine in rubber.

The mineral matter should also he determined by careful ignition, when the india-rubber of the sample is then obtained by difference.

The *sulphur of vulcanisation* can in this case be determined directly on a portion of the above residue from the alcoholic potash treatment by the method used for total sulphur (page 313); while the *chlorine of vulcanisation* may be determined on the remainder of the residue by one of the methods described on page 314.

The methods employed for the determination of the various constituents of manufactured rubber-goods are carried out as follows:—

Acetone Extraction.—Acetone dissolves oily and resinous substances without acting on india-rubber and vulcanised oils. A weight of two grammes of the sample is placed in an extraction-

[1] Weber's scheme of analysis, shortened in a similar manner to the method indicated in the text, is with one or two minor modifications recommended by Grimshaw, Tong and Barnes (*J. S. C. I.*, 1903, page 338).

thimble (Schleicher and Schüll), and extracted for about ten hours in a small Soxhlet apparatus (capacity about 50 c.c.). Weber prefers to use a form of apparatus in which there is a free annular space between an inner and an outer tube, through which the vapours of the solvent pass up into the condenser and fall down in drops again directly into the thimble. The material to be extracted is in this case kept at the boiling-point of the solvent, which continually drops away through the tube as soon as it has passed through the thimble. By means of this apparatus, the extraction is always complete in five hours and sometimes in a shorter period. Ether should not be substituted for acetone, as it has a slight action on the non-resinous constituents of rubber. Chloroform, benzene, and carbon disulphide also dissolve unvulcanised rubber, which is sometimes present in rubber articles. The amount of acetone extract may be taken as inversely proportional to the quality of the organic constituents of the rubber.

The general nature of the *extract* (which rarely exceeds 10 per cent. of the sample) will give sufficient indication of its composition, since a complete analysis may frequently be almost impossible. A light-coloured, clean-looking extract is obtained in the absence of substitutes, &c. If the extract is a more or less viscid liquid, solid hydrocarbons and resins are evidently absent. A liquid residue remaining on warming the extract with a small quantity of absolute alcohol will consist of mineral oil, which when present will have been noticed by the characteristic fluorescence of the acetone liquid. The proportion of the residue thus insoluble in absolute alcohol may be calculated as mineral oil. Resin oils may be detected by the purple coloration obtained with carbon disulphide and stannic bromide, or by the similar colour produced by acetic anhydride and sulphuric acid (pages 172, 177). The presence of mineral or resin oil may mean the presence of "recovered" rubber in the sample. Tallow also is sometimes present in the extract. If the warm alcohol deposits voluminous flakes on cooling, the presence of solid hydrocarbons (paraffin-wax, ceresin, ozokerite) is indicated.[1] Fatty oils may be determined approximately by saponifying the acetone extract with a known volume of standard alcoholic potash, titrating back the excess of alkali with standard acid (Koettstorfer's process). Since any fatty oil present consists, in the great majority of cases, of colza oil, every 0.172 gramme of KOH absorbed may be taken to represent one gramme of fatty oil in the extract.

[1] The effect of paraffin-wax on rubber is to protect the latter from oxidation, but a decided decrease in tensile strength is produced by the addition. A preparation named "Nantusi," used for mixing with rubber to prevent "suncracking," contains about 70 per cent. of paraffin-wax.

ANALYSIS OF ACETONE EXTRACT OF RUBBER.

<table>
<tr><th colspan="3">ACETONE EXTRACT SOLUBLE IN ALCOHOL.</th><th colspan="2">ACETONE EXTRACT INSOLUBLE IN ALCOHOL.</th></tr>
<tr><td colspan="3">Free fatty acids;
Resins (colophony);
Waxes (beeswax; carnauba);
Castor and blown oils.
Evaporate the alcohol, and treat the residue with 60 per cent. alcoholic chloral hydrate solution at 50° C.:—</td><td colspan="2">Fatty and mineral oils (except castor and blown oils);
Tar oils; solid hydrocarbons (paraffin-wax).
Shake the mixture in a separating funnel with 70 per cent. alcoholic chloral hydrate solution:—</td></tr>
<tr><td colspan="2">SOLUBLE IN CHLORAL HYDRATE.
Fatty Acids; Resins; Castor and Blown Oils.
Evaporate the solution to dryness, and treat the residue with 75 per cent. aqueous chloral hydrate solution:—</td><td rowspan="2">INSOLUBLE.
Waxes.</td><td rowspan="2">SOLUBLE IN CHLORAL HYDRATE.
Evaporate the separated liquid to dryness and weigh the residue of fatty oils.</td><td rowspan="2">INSOLUBLE.
Heavy tar oils; mineral oils; solid hydrocarbons.
Wash the insoluble matter into a flask with hot acetone, evaporate the solvent, and weigh the residue. Treat this residue with strong sulphuric acid, dilute the mixture with water and cool. A turbid homogeneous solution indicates the absence of mineral oil or wax, and the residue therefore consisted wholly of tar oils.
An oily layer floating on the acid liquid consists of mineral oil or paraffin-wax. Mineral oil may be separated from wax by glacial acetic acid.</td></tr>
<tr><td>SOLUBLE.
Resins.</td><td>INSOLUBLE.
Fatty bodies.
Dissolve in ether, evaporate the ethereal solution and weigh. The free fatty acids are then titrated.</td></tr>
</table>

(For explanation of this table see next page.)

The foregoing table shows C. O. Weber's method (*J. S. C. I.*, 1903, xxii, p. 576) for the detailed separation, by means of aqueous and alcoholic chloral hydrate solutions, of a complex mixture of substances occurring in the acetone extract of manufactured rubber. The residue left on evaporation of the acetone is boiled with absolute alcohol (see table on p. 299):—

It is unnecessary to distinguish between castor and blown oils, since they are of equal value in rubber mixtures. The former is practically insoluble in petroleum-spirit, the latter readily soluble.

For the determination of *free oily matters* and *paraffin-wax*, Heinzerling extracts the sample with oil of turpentine, carbon disulphide, or petroleum-spirit. The results are usually too high, owing to the presence of natural resins in rubber. Fatty oils added during manufacture may become partly changed by vulcanisation into the nature of substitutes, and cannot then be extracted by solvents. The addition of fatty oils as such to rubbers is very little practised at the present time, mineral or rosin oils being used. Fatty substitutes, however, invariably contain appreciable amounts of free fatty oils.

D. Holde determines *free fatty oils* in manufactured india-rubber by extracting one gramme of the finely-divided sample with 60 c.c. of ether-alcohol (4 : 3), the cold solvent being poured on to the rubber contained in a filter-paper. Henriques prefers to soak the comminuted rubber in half the total amount of cold ether-alcohol for one hour, then filter and wash with the remainder of the solvent, and weigh the residual rubber. Holde evaporates the filtered solvent and weighs the dried residue. Any mineral or resin oil present will also be found in the extract. A correction is required for the average amount of caoutchouc (5 per cent.) dissolved by the ether-alcohol. Holde states that he found the fatty substitutes to be insoluble in the above solvent (except that slight traces of sulphur were extracted), and that therefore the above method gives a separation of the free oils from the substitutes. Weber, however, states that the fatty matters present in commercial fatty substitutes are dissolved to a considerable extent (up to 20 per cent. and even more) in ether-alcohol (*J. S. C. I.*, 1894, page 476). Carbon disulphide containing 5 per cent. of alcohol will dissolve the free oil from substitutes.

For the determination of *unsaponifiable oils* in vulcanised rubber (*e. g.*, mineral oils, rosin oil and paraffin), R. Henriques (*Analyst*, 1899, page 297) extracts the residue from the rubber which has undergone the treatment with alcoholic soda (for the determination of substitutes) with ether by kneading in a mortar as long as the solvent is coloured. The loss of weight of the rubber-residue represents the unsaponifiable oils present.

In the presence of fatty oils or other foreign substances in the acetone extract, it is not possible to determine the amount of extract derived from the rubber of the sample, since the soluble matter from various rubbers varies greatly in character. It is thus impossible to differentiate between rubber resins and added resins. By experience it is possible to judge from the appearance of an extract whether it does or does not contain other substances than the resinous constituents of rubber. The amount of extract should be calculated on the india-rubber of the sample. All rubbers after hot vulcanisation contain from 3 to 5 per cent. more resinous matter than before vulcanisation.[1] If this be borne in mind, the amount of organic acetone extract obtained from any sample gives a clue to the class of rubber present in that sample. The acetone extract from a sample prepared from pure Para rubber never reaches 4.5 per cent., although it usually exceeds 3 per cent. The question as to whether a sample of rubber contains only Para rubber without admixture with other brands can therefore be decided by the amount of the acetone extract.

The acetone extract also contains the whole of the *free sulphur* of the sample, and its amount should be deducted from the total extract and expressed separately. The method for its determination differs according to the composition of the extract. If the sulphur crystallises from the acetone solution in well-shaped crystals, it is practically certain that the extract is free from any admixture of solid hydrocarbons or of oily or resinous matters other than those from the rubber itself. When this is the case, the acetone is distilled, the dried extract weighed, and the residue treated five times with 2 c.c. each of acetone, the liquid being filtered through a small filter into a weighed flask. The organic matter dissolves and leaves the greater part of the sulphur behind. Any sulphur which may have found its way on to the filter is dissolved out by washing the latter with 5 c.c. of carbon disulphide into the flask containing the main portion of the sulphur. The solvents are evaporated from the flasks and the dried residues weighed. A correction must be made for the solubility of sulphur in acetone, which amounts to 5 or 6 mgrms. in the 10 c.c. of acetone used. This amount should therefore be deducted from the organic residue and added to the sulphur residue. "Cold-cured" rubber goods yield only traces, if any, of free sulphur to the acetone extract.

When the original acetone extract is found to be a complex mixture, and especially if it contain hydrocarbons, Weber determines the sulphur by oxidising the total extract with fuming nitric acid on the water-bath, diluting with water, and pre-

[1] Rubbers vulcanised by the cold process show no appreciable increase in the proportion of resinous constituents.

cipitating the sulphate from the filtered liquid with barium chloride.[1]

Rubbers which have undergone deterioration owing to oxidation always contain increased amounts of resinous matters.

Pyridine Extraction.—The residue from the acetone treatment is used for the determination of tar (coal-tar, Stockholm tar), pitch and bituminous matters (asphaltum, &c.).

Henriques' method consists in digesting one gramme of the finely-divided sample (previously treated with alcoholic soda to extract free sulphur) with 30 c.c. of cold or slightly warm recently-distilled nitrobenzene for one hour, and the squeezed rubber washed with a further 30 c.c. of the solvent. The nitrobenzene immediately darkens in colour in the presence of tar, asphaltum, &c. The extract cannot be weighed direct owing to the high boiling-point of nitrobenzene. The loss of weight of the sample thus treated is therefore noted. The presence of mineral oils, paraffin-wax, and resins interferes with the determination of the asphaltum. According to Weber, however, the method is unreliable, owing to the fact that, contrary to Henriques' ideas, pitch, asphaltum, &c., frequently contain considerable amounts of matter insoluble in nitrobenzene. For this reason, Weber prefers an extraction with pyridine, the residue in the extraction-thimble from the acetone treatment being employed. 60 c.c. of pyridine (b. pt. 109° to 111° C.) is placed in a weighed flask, and the extraction begun immediately the flask containing the acetone extract has been disconnected. The solvent is heated by means of an oil-bath kept at 116° to 120° C., when in the presence of any tar, pitch, &c., the paper thimble at once becomes dark coloured, and the extraction is then continued until nothing more is dissolved out. The pyridine is finally distilled at the temperature of the oil-bath (a sand-bath would cause overheating towards the end of the distillation), the flask carefully cleaned on the outside to get rid of the oil, and the residue then dried at 100° C. until all odour of pyridine has disappeared, and finally weighed.

The character of the pyridine extract will probably give the clue to its nature. Tar is a black viscid liquid, pitch consists of a ductile black mass, and asphaltum is a brittle, dark brownish-maroon substance. If more than one of these substances be present, their recognition would be a difficult matter, but

[1] The author has found that treatment with nitric acid does not suffice to destroy all the resinous matter, &c., of rubber, and thus the barium sulphate obtained as described in Weber's process will usually be contaminated with barium carbonate (from the ignition of barium salts of resin-acids. (See also R. Henriques, *J. S. C. I.*, 1893, p. 467.) It would therefore be preferable to treat the acetone extract, after being oxidised with nitric acid as above, in the same way as in the determination of sulphur in the pyridine extract (page 303).

the separation is not of any importance. The addition of tar and pitch to rubber mixings serves the purpose of softening the rubber, and so does away with an undesirable amount of mechanical working. When thus softened, the rubber can readily take up large quantities of mineral matters. The proportion of tar, &c., usually added to rubber-mixings does not exceed one per cent. Asphaltum is not much used for soft rubber goods, and does not appear to possess any advantage over many other organic admixtures.

The sulphur in the pyridine extract is present in organic combination, and cannot be determined by the method used in the case of the complex acetone extract, since the sulpho-acids which may be produced are not precipitated by barium chloride. The extract in the flask is therefore oxidised on the water-bath with fuming nitric acid, and when solution is complete, it is transferred by washing out with hot fuming nitric acid to a small porcelain basin. The liquid is concentrated to a syrup, half a gramme of pure sodium acetate added, and the mixture evaporated to dryness, and ignited with the aid of small quantities of sodium nitrate. The cooled mass is dissolved in hot water, the solution filtered, and in the filtrate after acidification with hydrochloric acid, the sulphate is precipitated with barium chloride.

The residue from the pyridine extraction is washed with acetone to free it from pyridine, when it is transferred to a flask, and examined by Henriques' process for the presence of fatty substitutes (rubber surrogates). These substitutes consist of chlorosulphides, sulphides or oxides of fatty oils (triglycerides), and they are consequently saponifiable (see page 318). The process is carried out in the author's laboratory in the following way:—Two grammes of the finely-rasped rubber is boiled in a flask on the water-bath twice for three hours consecutively with two quantities of 50 c.c. each of 6 per cent. alcoholic soda solution.[1] The residual rubber is transferred to a weighed filter-paper and washed with hot water until the washings are neutral to litmus-paper.[2] The washings are added to the alcoholic soda extract. Owing to the fact that rubber when boiled with alcoholic soda solution in the above manner always retains, after washing,

[1] Care should of course be taken that the caustic soda employed in making the alcoholic soda solution is quite free from *sulphur* in any form.

[2] It has been pointed out by R. Thal (abst. *Analyst*, 1899, page 16) that an appreciable error is introduced into the process unless account is taken of the solvent action of the alcoholic soda solution and washings upon the tared filter. The use of the weighed filter-paper is necessary in all cases where the rubber contains mineral matters. In the absence of any notable quantity of inorganic compounds in the rubber, the partly-dried rubber residue on the filter may be transferred to a watch-glass, dried, and weighed.

considerable quantities of alkali (6 per cent.) in an insoluble form, Henriques directs that the rubber residue be boiled with dilute hydrochloric acid several times, which treatment removes the greater part of this combined alkali. It has been found by Weber, however, that the alkali is not absorbed by the rubber matter itself, but by its resinous constituents, forming sodium salts with the acids. When, therefore, the rubber-resins have been previously removed by an extraction with acetone, as in Weber's scheme, the alkali can be practically all eliminated by washing with hot water, and no treatment with acid is necessary.[1] This is a great advantage in the case of rubbers containing mineral matter, since the acid treatment frequently dissolves out all or part of the inorganic constituents, and thus renders their subsequent determination much more complicated. The pure rubber matter, thus washed free from alkali by hot water, is then dried in a flask at 100° in a current of coal-gas. Direct drying in air at 100° causes oxidation of the rubber, which may seriously affect the results. The dry rubber is finally weighed in the flask, the loss of weight by the saponification treatment representing the fatty substitutes present. Alcoholic soda solution has, however, a slight action upon rubber, dissolving on the average about 2.5 or 3 per cent. of vulcanised rubber, and this is therefore allowed for in the calculation.[2] The amount of rubber substitutes found should be calculated on the original sample, and afterwards if desired on the organic matter of the sample. Since the alcoholic soda extract contains all the free

[1] The author follows Henriques' complete method in cases where the acetone treatment has not, for any reason, preceded the saponification with alcoholic soda. The rubber is washed until the washings are neutral to litmus-paper and then boiled repeatedly (about 5 times) with dilute hydrochloric acid (1 : 20) The pure rubber is transferred to a filter and washed first with hot water until free from acid, and finally with alcohol to assist the subsequent drying in the steam-oven. To obviate the error due to loss of mineral matter by this treatment with acid, the pure rubber matter after weighing is next incinerated, and the ash thus obtained deducted from the weight of extracted rubber. The insoluble residue after the saponification treatment, *less* the mineral matter and sulphur present in it, gives the real rubber matter of the sample. (This cannot, however, give accurate results in the case of samples containing mercury compounds or other volatile metallic constituents or carbonaceous matters, unless these are separately determined and allowed for.) If now from the total volatile matter (100-Ash) *less* total sulphur, is deducted the percentage of real rubber in the sample, the percentage of alcoholic soda extract (fatty substitutes) is obtained, and this should be calculated also on the organic matter of the sample.

[2] Working in the author's laboratory, A. R. Tankard obtained the following amounts of alcoholic soda extract from samples of pure Para rubber examined by Henriques's complete method:—

Washed unvulcanised Para, ...	2.73 per cent.
Vulcanised Para, ...	3.20 " "

sulphur of the sample, Henriques has proposed the determination as a means of arriving at the sulphur of vulcanisation, by difference from the total organically-combined sulphur.

The method of calculation of the amount of rubber substitute present in rubber is carried out as follows (R. Henriques, *Analyst*, 1894, page 111). The correction for the average solubility of rubber in alcoholic soda solution (2.5 per cent.) is included:—

If x = Percentage of India-rubber, y = Percentage of Fatty Acids } in the sample.

Then:— $x = \frac{100}{97.5}(c - d - e)$,

and $y = 100 - (a + b + x)$,

where:—
a, = Total Sulphur.
b, = Total Ash.
c, = Residue from alcoholic soda treatment.
d, = Sulphur in (c).
e, = Ash in (c).

The amount of sulphur in the substitute present is obtained by calculation in the following way. The sulphur-content of white substitute is equal to that of its fatty acids, and the sulphur-content of brown substitute is (on the average) 1.5 per cent. higher than that of its fatty acids. Therefore the sulphur in the alcoholic soda extract is determined, and the difference between the total sulphur and the sulphur in the substitute (calculated according to its nature, pages 306, 322) gives the sulphur used for vulcanisation. Of course, this includes the free sulphur, and any sulphur present in the mineral matter of the sample must be allowed for separately.

In order to ascertain the kind of substitutes present in manufactured rubber, the *chlorine and sulphur in the alcoholic soda extract* must be determined.[1] These values are also required to obtain a knowledge of the extent of vulcanisation of the sample. For these determinations, the alkaline alcoholic liquid, with the washings, is evaporated to about 50 c.c., and then made up to a volume of 100 c.c. The chlorine is determined by evaporating 50 c.c. of this liquid to dryness, and igniting the residue with the aid of sodium nitrate until all carbon has disappeared. This residue is dissolved in water, the solution acidulated with nitric acid, and any chlorine present precipitated

[1] According to C. O. Weber, when white substitute (a chlorosulphide) is used for the hot vulcanisation of rubber goods, as is sometimes the case, it loses more or less of its chlorine in the form of hydrochloric acid, the whole of which is retained by the rubber, a portion of the chlorine combining with the latter with formation of a polyprene hydrochloride; while, in the presence of such substances as litharge and calcium carbonate, &c., the remainder is taken up by the mineral matters. The dechlorination of the substitute is, however, far from complete, and the presence of chlorine in the substitute cannot escape detection (see page 322).

with silver nitrate and weighed in the usual way. The sulphur is determined on the remaining 50 c.c. of the original solution by treating it with bromine or bromine-water on the water-bath to oxidise the alkaline sulphides present. The liquid is then evaporated to a syrup, oxidised with fuming nitric acid, evaporated to dryness and ignited as before. The residue is dissolved in water, and the sulphate precipitated with barium chloride.

The following deductions from the results of the above methods of analysis have been made by R. Henriques (*J. S. C. I.*, 1894, page 70). The presence of chlorine and sulphur in approximately molecular proportions (=about equal weights) in the alcoholic soda extract indicates the presence of white substitute (chloro-sulphide), or a mixture of this with blown-oil substitute. If the sulphur is considerably in excess of this molecular ratio, then both white and brown substitutes are present in the extract, with possibly also blown-oil substitute. When sulphur only is present, and no chlorine, the substitute employed is the brown variety, or a mixture of this with blown-oil substitute. If the extract is due to the "brown" substitute alone, it will contain about 10 per cent. of sulphur, whereas at most only traces of this element are present in a blown-oil extract. The absence of both sulphur and chlorine in the extract indicates, in the presence of a substitute, that one prepared from blown-oil has been added. It is impossible to distinguish between fatty oils added during manufacture (and which have therefore been vulcanised and become of the nature of fatty substitutes) and the true substitutes added as such.

The *residue from the alcoholic soda extraction* is treated with some solvent to separate the india-rubber from the mineral matter. R. Henriques has proposed to dissolve out the former by treatment with boiling petroleum (fractions of petroleum spirit boiling between 140° and 250° F.). According to Weber, however, this solvent only attacks very lightly vulcanised rubber.[1] The use of nitrobenzene suggested by the latter was subsequently found to be open to a similar objection, though to a smaller degree, but its greatest disadvantage lay in the fact that the resultant solutions were frequently either difficult

[1] The method of extraction of the sample with boiling petroleum was suggested by Henriques for the separation and determination of the free sulphur and sulphur of vulcanisation and that present in the mineral constituents (*J. S. C. I.*, 1893, page 467). The method is, however, tedious, and in many cases—as, for instance, when much mineral matter is present—the solution of the rubber is incomplete. Henriques has therefore abandoned the use of this solvent (*Analyst*, 1894, page 111) and finds it preferable to decompose the sulphides in the finely-rasped sample with acid, and to determine the sulphur of the sulphides and that of the sulphates as described on page 313. The residue contains sulphur in the form of vulcanising sulphate and insoluble sulphates (of lead and barium), which latter can be allowed for by calculation from the bases.

or impossible to filter,[1] especially if the mineral matter consisted of antimony sulphide or zinc oxide. It is important to obtain a method by which the rubber can be conveniently dissolved and separated from the mineral matter, since the incineration of the sample causes loss of various volatile constituents (mercury and antimony compounds), carbonic acid is driven off from carbonates, carbon pigments, carbohydrates and fibre are burnt, and so on. Weber has therefore suggested the use of a-nitronaphthalene, which quickly decomposes and dissolves the rubber of samples heavily vulcanised, and gives solutions which, when diluted with benzene and allowed to stand for a few hours, filter readily and give clear filtrates.

Another disadvantage of the nitrobenzene treatment, which also applies to the nitronaphthalene method, is the carbonisation of the rubber matter at the high temperature employed when the sample under treatment contains red lead or ferric oxide. In the case of nitrobenzene, the difficulty can be avoided by the addition of a small quantity (5 per cent.) of chloroform, which reduces the temperature from 208° to about 173° C.[2] In the case of nitronaphthalene, however, only an insignificant lowering of the boiling-point takes place by the addition of chloroform, and Weber prefers to use a specially-made air-bath,[3] standing on a tripod, and having a thin layer of fluffy asbestos-fibre placed on the bottom of the inside. The weighed residue of rubber and mineral matter (from the alcoholic soda treatment), together with about 60 grammes of a-nitronaphthalene, are placed in a weighed wide-necked flask, which is suspended from the lid of the bath in such a way that it does not come into contact with the sides or the bottom of the bath. The temperature is kept at 180° C. A higher temperature may cause carbonisation of the rubber. The solution of the ruhber is usually complete in an hour, and sometimes a much less time suffices. During the heating the contents of the flask should be frequently stirred gently with a glass rod. When solution is complete the flask and its contents are *allowed to cool*, about 150 c.c. of benzene is added, and the liquid left to stand until

[1] This is in accord with the experience of R. Henriques and of the author.

[2] C. O. Weber obtained, by the nitrobenzene treatment on two samples of manufactured rubber, a considerable amount of carbonaceous matter left with the mineral matter after the rubber had been dissolved out. The mineral matter left contained lead oxide, PbO. When the samples were examined by the nitrobenzene-chloroform method, however, no carbon was obtained, and the mineral matter contained lead peroxide, PbO_2, added to the samples as red lead. At the boiling-point of nitrobenzene, lead peroxide undoubtedly oxidises the india-rubber, with production of carbon and lead oxide, PbO.

[3] Obtainable from Messrs. F. Jackson & Co., 11, Half Moon Street, Manchester.

the mineral matter settles out. The solution is then filtered, the residue on the filter being finally washed with benzene, dried at 110° for one hour, and weighed.

The loss of weight by the nitronaphthalene treatment represents the india-rubber of the sample, including the sulphur and chlorine of vulcanisation. The nitronaphthalene solution of the india-rubber does not, however, contain rubber as such, since this has undergone decomposition by the treatment,[1] and cannot be recovered from the nitronaphthalene.[2] For this reason the sulphur and chlorine of vulcanisation cannot be directly determined on this solution.

An alternative method for the determination of the india-rubber and its separation from mineral matter, by means of nitrogen tetroxide, is described on page 309. It may be conveniently applied to the residue from the alcoholic soda process.

It is almost impossible at present to determine the proportion of "recovered rubber" in rubber goods, and very difficult to detect its presence. Although in commerce recovered rubber is known as "devulcanised rubber," Weber affirms that it not only contains the whole of the sulphur of vulcanisation of the waste rubber from which it was obtained,[3] but also undergoes further vulcanisation in the process of recovery, and therefore a sample containing any quantity of this material will frequently have a high "coefficient of vulcanisation" (Weber). This "coefficient" is the percentage ratio between the amounts of india-rubber and sulphur of vulcanisation of the sample. Thus, if a sample has been found to contain 50 per cent. of real rubber matter and 2 per cent. of vulcanisation sulphur, its "coefficient of vulcanisation" will be 4 per cent. Weber suggests this

[1] The decomposition-product is stated by Weber to be similar to caoutchouc, in that it forms an additive compound with bromine, $C_{10}H_{16}Br_4$, which is quantitatively precipitated by alcohol.

[2] The presence of guttapercha or balata in vulcanised rubber cannot, therefore, be detected by this method of analysis. In rubber articles only slightly vulcanised, guttapercha and balata can be extracted, according to Weber, by repeated treatment of the original sample with cold benzene, and precipitation of the benzene extract with absolute alcohol. The advantage of mixing these substances with rubber is very doubtful, and they are rarely present to the extent of more than 1 or 2 per cent.

[3] R. Henriques (*J. S. C. I.*, 1894, p. 407), however, states that in the regeneration of rubber by the "recovery" process, actual devulcanisation seems to take place by oxidation. That such is the case is, according to Henriques, shown by the fact that regenerated rubber possesses the plastic properties of natural caoutchouc to some extent, and also on analysis of a "recovered" sample, a large quantity of sulphates was found to be present, and but little sulphur in organic combination. An examination by Henriques of further samples containing only about 50 per cent. of real rubber showed, however, a proportion of sulphur of vulcanisation ranging from 0.71 to 2.03 per cent.

coefficient as the basis for an approximate determination of recovered rubber.

The composition and properties of recovered rubber are described on page 324.

When the usual methods of analysis offer any special difficulty, Weber employs the following process, which he found to give excellent results in the case of a sample of highly-vulcanised rubber containing 50 per cent. of chalk and lead oxide. (See *Analyst*, 1904, p. 53.) The sample is extracted with acetone, and then dried in a current of carbon dioxide or coal-gas. The rubber is next suspended in dry chloroform or benzene, and a current of nitrogen peroxide (prepared by heating lead nitrate, and dried by means of glacial phosphoric acid) passed through the liquid until it acquires a deep red colour. The rubber is converted into a bright yellow friable mass, the compound having the composition $C_{10}H_{16}N_2O_4$ (Weber). After standing for about an hour, the chloroform or benzene solution is filtered, the residue washed with small quantities of the same solvent, and finally dried at 50°. The dry nitro-compound is then treated with warm acetone, in which it quickly dissolves. Solution may be hastened by warming on the water-bath if necessary. The mineral and albuminous matters remain insoluble, and after the liquid has been allowed to stand for a short time,[1] it is filtered, the mineral matter, &c., being washed with acetone, dried, and weighed. The filtrate, with the washings, is poured into a 10 per cent. aqueous solution of ammonium chloride,[2] and the precipitated nitro-compound washed with hot water, dried at 60°, and weighed. Any sulphur and chlorine of vulcanisation present in the sample must be determined in the usual way, and the amounts deducted from the weight of the nitro-compound. The caoutchouc present can then be calculated from the weight of the nitro-compound (*minus* its sulphur- and chlorine-content), which contains 59.65 per cent. of pure rubber; or 100 parts of caoutchouc produce 167.6 parts of the nitro-compound (see page 282).

[1] The mineral constituents usually settle well from the acetone solution, but antimony, mercury, and zinc sulphides may remain suspended in the liquid and pass largely through the filter. If, however, a small quantity of a solution of ammonium thiocyanate in acetone be added to the turbid liquid, a clear filtrate will be obtained. Centrifugalisation of the solution before filtration is sometimes necessary.

[2] Water cannot be employed to precipitate the nitro-compound in the case of vulcanised rubber, since the product is obtained in the form of a thick yellow oil. In the case of unvulcanised (raw) rubber, the filtrate and washings from the mineral matter are mixed and poured into eight times the volume of water, when the nitro-compound falls as a fine flaky yellow precipitate. This is filtered off, washed with lukewarm water, dried at a temperature not exceeding 90° C., and weighed.

C. Harries (*Ber.*, 1903, xxxvi, 1937; abst. *J. S. C. I.*, 1903, page 875) employs dry nitrous acid gas instead of the nitrogen peroxide used by Weber, the resultant "nitrosite" having, according to Harries, the composition $(C_{10}H_{15}N_3O_7)_2$. The method of procedure is substantially that of Weber (see page 309). Alexander and others consider these methods unreliable owing to the varying composition of the addition-products obtained. Further investigation is desirable.

The *residue from the nitronaphthalene treatment* may contain carbohydrates, fibrous materials, mineral matters, and the sulphur of the mineral constituents. (Cork and wood-refuse are now practically never used in rubber manufacture.) The residue on the filter is therefore washed with boiling water (about 200 c.c.) in small quantities at a time, which will remove all dextrin or soluble starch, and which may be detected in the filtrate by iodine. The previous treatment with nitrobenzene or nitronaphthalene will have converted any starchy matter into solnble starch or (chiefly) dextrin. If either of these substances, which are simply filling materials, is found the loss of weight, after drying the residue, should be noted. In order to ascertain whether dextrin or starchy matter was added to the rubber originally, a little of the sample is boiled with water for a few minutes, and a few drops of a solution of iodine added to the cooled liquid. Dextrin is only very rarely employed. It should be remembered that certain mineral constituents may be partially soluble in water (calcium sulphate, &c.).

The *residue from the treatment with boiling water* should be carefully examined under the microscope for animal or vegetable fibres. These when present can be separated from the mineral matter, if their determination is of sufficient importance, by shaking up a known weight of the residue with chloroform. Weber recommends that the operation be carried out in a test-tube, gently shaking the residue with about 20 c.c. of chloroform. and allowing the liqnid to stand, occasionally tapping the tube. When the mineral matter has settled and the fibres have risen to the top, a pipette containing chloroform is dipped under the surface of the chloroform in the tube, which is then held in an inclined position, and the chloroform in the pipette allowed to flow out. The chloroform in the tube will overflow, carrying the fibres with it, and they should be received in a dish, the chloroform being subsequently evaporated and the residue of fibres weighed. The amount of fibre in the whole residue is then calculated.

The presence of carbon (lamp-black, &c.) in the residue from the water extraction will be recognised by its appearance. It may be determined on a portion of the residue by combustion

with lead chromate. Any graphite or other carbonaceous matters present will also be included.

Henriques proposes to determine *lamp-black* in rubber goods containing only oils, rubber substitutes, and asphalt in addition, by *exhausting the substance successively with boiling alcoholic* soda and cold nitrobenzene, and submitting the residue to combustion. India-rubber contains carbon and hydrogen in the proportions 10 : 16, so that any admixture of carbon with the rubber can be determined by means of the altered proportions between the carbon and hydrogen. Henriques' method is regarded by Weber as quite unreliable; whilst in cases where other carbonaceous matters, in addition to lamp-black, are present in rubber (*e. g.*, Vandyke brown, fibrous materials, &c.), the method is obviously inapplicable. The proportion of lamp-black present in rubber is usually not more than 1 per cent. Weber has found that by making up a similar mixture of the mineral matters to that found in the rubber, and blending this mixture with varying amounts of lamp-black until the shade of colour is equal to that of the sample, an approximate determination of the amount of lamp-black may be obtained.

A. Heintz (*Analyst*, 1902, xxvii, 200) has suggested the direct determination of the caoutchouc in manufactured rubber by combustion of the rubber matter left after other organic substances have been removed, the water produced being weighed. The unsaponifiable oils, asphalt and rubber snbstitutes are extracted by the usual solvents, and the well-washed and thoroughly dried rubber residne burnt, the snlphur being kept back in the usual way. The amount of caoutchonc present may then be calculated from the hydrogen found on the assumption that its composition is represented by the formula $C_{10}H_{16}$. The results are only approximate, since the caoutchouc contains usually about 3 per cent. of an oxygenated body, but this may be allowed for in the subsequent calculation. Further evidence would seem to be necessary to show that caoutchouc, after having been mixed during manufacture with various other ingredients, still approximates to the composition $C_{10}H_{16}$.

The determination of the various mineral constituents of the residue is carried out in the usual way.[1] According to Weber,

[1] In some cases, as, for instance, when the mineral matter has been largely used up in a qualitative examination, the mineral matter may be best obtained for quantitative purposes by decomposing a known weight of the original sample with hot nitric acid, evaporating the liquid to dryness, and adding a few drops of sulphuric acid. The excess of acid is driven off by heating the residue on a sand-bath, and the analysis proceeded with by the ordinary methods. If preferred, the original rubber, after treatment with acetone, may be decomposed by the nitrobenzene (or nitronaphthalene) extraction method, and the mineral matter, obtained by filtration of the liquid, treated as desired. Weber recom-

the most usual inorganic substances employed are, in the order of their importance:—Litharge; Paris white, whiting, $CaCO_3$; zinc white, ZnO; lime; barium sulphate; Orr's white, or "lithopone," which is a mixture of zinc sulphide and oxide with barium sulphate; golden sulphide, Sb_2S_5; lamp-black; magnesia; red lead; ferric oxide, and French chalk. In addition to these: china clay; vermilion; plaster of Paris; gypsum or pearl white; white lead; kieselguhr; zinc sulphide; lead sulphide, thiosulphate and sulphate; graphite; magnesium carbonate; pumice-stone powder; glass powder; mica; arsenious sulphide; zinc dust; aluminium powder; iron and brass filings, and asbestos are also used. The microscopical examination of the mineral matter will frequently give much useful information as to its composition.

The *total sulphur in the mineral matter* is determined in the following manner:—A weighed quantity of the residue obtained above (residue K, see table on page 296) is added in small quantities at a time to about 10 c.c. of fuming nitric acid contained in a small evaporating basin, which is covered by a clock-glass to avoid loss. The watch-glass on which the mineral matter is weighed out is cleaned from the last portions of the mineral matter by means of small pieces of moist-filter paper, which are added to the acid. The whole is evaporated to a syrup, 20 c.c. more nitric acid added if necessary, and the evaporation repeated until most of the acid has been driven off. Two grammes of pure sodium acetate is now added and the contents of the basin evaporated to dryness.[1] The residue is carefully

mends this course in the analysis of samples yielding easily to the nitrobenzene treatment.

The presence of copper in rubber goods is very undesirable, owing to its deleterious influence on the rubber, especially in the case of cold vulcanised (sulphur chloride) goods. In such cases the copper, even when present in very small quantity, is converted into cupric chloride, which dissolves in the resinous and oily substances present in rubber goods, and therefore permeates the whole material, and gradually hardens and destroys the rubber.

For the detection of small quantities of copper in rubber goods, C. O. Weber ignites two or three grammes of the sample in a porcelain crucible till all carbonaceous matter is destroyed. The ash is moistened with a few drops of nitric acid, dried, and heated to redness for a few minutes. It is then treated with a slight excess of dilute sulphuric acid, the solution filtered and the residue washed with a small quantity of boiling water. The filtrate is neutralised (or left very faintly acid) with caustic soda, and tested with zinc sulphide paper. The method is stated to be more sensitive than the ferrocyanide test, allowing of the detection of 0·007 per cent. of copper.

[1] It would be preferable at this stage to make an addition of a little sodium carbonate to ensure the presence of an excess of alkali, which on fusing causes the complete decomposition of any barium or lead sulphate in the inorganic matter. Henriques makes an addition of 5 grammes of a mixture of sodium carbonate and potassium nitrate (5 : 3) in place of

ignited, and the carbonaceous matter burnt by the addition of a few small crystals of potassium nitrate. When graphite is present, prolonged fusion may be necessary. The mass is kept fused for a short time, and after cooling is dissolved in boiling water, filtered from oxide of iron, carbonates of lead, barium, &c., and the sulphuric acid in the filtrate precipitated by the addition of hydrochloric acid and barium chloride in the usual way. The sulphur thus found is calculated first upon the mineral matter and finally upon the original sample.

For the determination of the sulphides and sulphates in the mineral matter, R. Henriques (*J. S. C. I.*, 1900, p. 177) boils a portion of the inorganic residue with hydrochloric acid, filters, and determines the sulphur in the insoluble residue. Any soluble sulphates will be in the acid solution. The difference between the total sulphur in the mineral constituents and the sulphur present in the insoluble residue represents that present in the form of sulphides. Sulphur present as sulphates is determined in the usual manner in the insoluble residue.

Determination of Total Sulphur.—The processes of R. Henriques and of C. O. Weber are very similar, and are carried out as follows: About 2 grammes of the sample, cut up into small pieces, is treated on a warm water-bath with about 15 c.c. of pure strong nitric acid, the rubber being added to the acid in small quantities at a time. The method is then carried out as in the determination of sulphur in the mineral matter.

The following is a reliable and rapid method for the determination of total sulphur in rubber and rubber goods:—

The finely-divided rubber is intimately mixed with a sufficient quantity of sodium peroxide and introduced into a metal vessel

the sodium acetate employed by Weber. Care should be taken that the melt is not too strongly alkaline or it will unduly attack the basin. Henriques treats the fused mass with water and hydrochloric acid, and evaporates the liquid to dryness to render any silica insoluble, when nitric acid is added and the liquid filtered. Any lead sulphate present is subsequently extracted from the siliceous residue by means of boiling ammonium acetate solution and added to the main quantity of liquid. The sulphate in the solution is then precipitated by barium chloride. Barium sulphate in the siliceous residue is determined as usual. Samples containing cinnabar should be treated with nitric acid as described in the text, the liquid diluted with water and filtered, and sulphuretted hydrogen passed through the solution.

In the determination of sulphur by Henriques' process the presence, in the mineral matters of the sample, of metals capable of forming nitrates may produce deflagration, and consequent loss of sulphur, owing to the explosive violence of the reaction. Weber, therefore, considers Carius' sealed-tube method preferable (with the rubber and nitric acid), the tube being cautiously opened after one hour's heating, resealed, and then the heating continued as before. The method is very accurate, but it should be borne in mind that any insoluble residue may contain sulphur in the form of barium, calcium or lead sulphates.

(known as the cartridge), which is surrounded with water. A red-hot wire is then dropped into the mixture, which is immediately ignited. The heat generated is sufficient to entirely fuse the mixture, and to destroy the organic matter. The fused mass is dissolved by boiling with water, and the liquid acidified with hydrochloric acid. The solution is finally boiled, filtered if necessary, and the sulphate determined by precipitation with barium chloride.

The *sulphur of vulcanisation* may now be calculated, from the results of the various sulphur determinations, by subtracting the sum of the sulphur found in various forms from the total sulphur of the sample.[1] Owing to the importance of this figure, however, it is desirable to obtain a more direct determination. This may be done by reproducing the residue F (page 296) by means of the necessary extractions on about one gramme of the sample, determining the total sulphur in the residue by the process used for the determination of total sulphur, and subtracting from the result obtained, the amount of sulphur found in the mineral matter, which gives the sulphur in the rubber.

The *chlorine* in a sample of rubber may be determined by Carius' well-known sealed-tube method, using about 0.3 gramme of the sample,[2] together with 5 c.c. of fuming nitric acid and one gramme of silver nitrate. Most rubbers contain mineral matter insoluble in nitric acid, and when this is the case, the mixture of silver chloride and insoluble mineral matter may be treated with dilute sulphuric acid and metallic zinc in a platinum vessel, the liquid being frequently stirred. When the decomposition of the silver chloride is complete, the liquid is filtered or decanted from the insoluble matter, and the chloride precipitated, or titrated with silver nitrate.

A more convenient process for the determination of chlorine consists in oxidising the rubber by very careful fusion in platinum with a mixture of two parts of sodium carbonate and one part of potassium nitrate. The product is dissolved in water, and the chloride in the filtered liquid determined as silver chloride.[3]

[1] In the case of rubbers free from mineral matter, or of rubbers the mineral matter of which is free from sulphur, a direct determination of the sulphur of vulcanisation can be made (see page 297).

[2] Samples containing chlorosulphide substitutes must be first treated with alcoholic potash as already described, and the chlorine determined as above on the residue.

[3] A similar method has been proposed for the determination of the total sulphur in rubber, the sulphate in the filtrate being precipitated by barium chloride. The results obtained are, however, quite valueless, a large amount of the sulphur present being volatilised in the form of organic sulphides.

A general examination of the original rubber will frequently give valuable information as to the composition of the mineral matter present, and the form in which it occurs. Grey rubber contains no colouring-matter. Red rubbers may contain antimony pentasulphide, mercuric sulphide or ferric oxide.[1] Black rubbers are desulphurised "cut-sheet" articles or goods containing lamp-black, pitches and similar compounds. Water may dissolve out certain constituents, such as calcium sulphate, from the finely-rasped sample. Weber found 6 per cent. of sodium carbonate in a sample of rubber. Hydrochloric acid may separate other substances. The presence of lead sulphate in rubber may be detected and its amount determined by boiling a known weight of the finely-divided (rasped) sample with ammonium acetate solution for about half an hour, and precipitating the lead from tbe solution after filtration. Barium sulphate when present will of course remain insoluble in hydrochloric acid with the siliceous portion of the mineral matter, and may be separated from the latter by fusion with alkaline carbonates in the usual way.

Carbonic acid in the mineral matter (which frequently occurs as calcium, lead, zinc, and magnesium carbonates) may be determined in vulcanised rubber articles, by treating the finely-rasped sample (cutting will not suffice) in a Geissler or similar apparatus with dilute hydrochloric acid in which a small quantity of cupric sulphate has been dissolved. This serves to retain the sulphuretted hydrogen from any sulphides which may be present. In the case of non-vulcanised rubber, the caoutchouc must be removed (wholly or partially) by treatment of the sample with boiling nitrobenzene, and a portion of the powdered residue treated as above. It is advisable to follow this method even in the case of vulcanised rubber.

In the case of rubbers containing carbonates and sulphides, these constituents may be determined separately as already described, or by determining the total gases (by loss) given off when the finely-divided sample is treated with hydrochloric acid in the usual manner, and subtracting the sulphuretted hydrogen evolved (previously found). The difference represents the carbonic acid in the sample.

O. Chéneau (*Analyst*, 1900, xxv, 235) has published a systematic method for the analysis of manufactured rubber, in

[1] Attention has recently been called to the possibility of antimonial contamination of aërated waters through the red rubber rings on some kinds of bottles. The insoluble form in which antimony occurs in rubber makes it an unlikely impurity except in traces (which have indeed been found in certain waters), but the use of antimony-containing rubber for such purposes is undesirable and should be avoided.

which the usual well-known solvents suggested by Henriques and Weber for the separation and determination of the various ingredients of rubber goods are employed. Previous to a treatment of the sample with alcoholic soda, Chéneau warms a weighed quantity of the rubber with dilute acetic acid to which some cane-sugar has been added. This removes calcium, lead, zinc and magnesium carbonates; lime and zinc oxide; red lead; white lead; alkalies; and any starch present in the sample. Any sulphuretted hydrogen evolved by the acetic acid treatment is due to the presence of ultramarine or other sulphide decomposable by acetic acid, and its amount should be determined.

Analysis of Hard Rubber.

While highly-vulcanised samples of soft rubber are difficult to dissolve by the nitrobenzene or other process (page 306), hard rubber goods, such as ebonite, are quite insoluble in any known solvent.

Hard rubbers never contain any admixture of fatty substitutes, although in addition to rubber and mineral matter, certain resins and pitches are frequently present. C. O. Weber (*Chemistry of India-rubber*) gives the following scheme of analysis for hard rubber. The sample is filed to a very fine powder,[1] and about two grammes of the well-mixed powder extracted with hot acetone for about two days, in the manner described on page 297. This prolonged treatment in the case of hard rubber goods is absolutely necessary to ensure complete extraction.

(A) Soluble in Acetone.	(B) Residue. Extracted with Epichlorhydrin.		
Rubber Resins. Added resinous bodies. Free Sulphur.	(C) Soluble in Epichlorhydrin.	(D) Residue. Extracted with Pyridine.	
	All resins insoluble in Acetone. Sulphur in above.	(E) Soluble in Pyridine.	(F) Residue.
		Bituminous bodies. Pitches. Sulphur in above.	Sulphur in residue.

[1] The powdered sample should preferably be passed through a sieve having 80 to 100 meshes per square inch. The portions not passing through should then be re-ground and passed through the sieve again, this being repeated until all goes through the sieve.

Separate determinations should also be made of the mineral matter (by ignition) and of the sulphur in the mineral matter.

The acetone extract usually consists largely of sulphur, and this may be determined by oxidation with fuming nitric acid. When the amount of organic acetone extract (total acetone extract *minus* sulphur) exceeds 4 per cent., it is probable that added resinous bodies are present in the sample. The detection of the particular resin or resins present is a very difficult and usually impossible task.

The residue from the extraction with acetone is next subjected to the action of epichlorhydrin in the extraction-apparatus. It is not necessary to dry the residue after extraction with acetone, a flask containing about 75 c.c. of epichlorhydrin being attached to the apparatus as soon as the first extraction is completed. The extraction with epichlorhydrin is continued for about three hours. The flask must be heated upon a sand-bath or asbestos-coated wire-gauze, since epichlorhydrin boils at 117° C. Dichlorhydrin may be used instead of epichlorhydrin, but the boiling-point of the former is very high (177°), and therefore epichlorhydrin is the preferable solvent. These two solvents dissolve a large number of resins which are partially or wholly insoluble in acetone, as, for instance, amber, copal, dammar, mastic, shellac, &c. These resins, together with acaroid, benzoin, colophony, elemi, and sandarac, which are soluble in acetone, constitute the chief resinous constituents of hard rubber goods. Shellac and amber are most frequently employed. The resins are soluble in alcohol, while the waxes and pitches (boiled tar, stearin pitch) are insoluble. The waxes (paraffin-wax, ceresin and ozokerite) are fairly soluble in acetone (page 299), while the pitches are partially soluble in acetone and in cold nitrobenzene. Asphaltum and sulphuretted stearin-pitch (Callender's bitumen) are fairly soluble in warm nitrobenzene.

The epichlorhydrin is distilled from a paraffin-bath kept at about 120° to 122°, and the residue finally dried for two hours at 110°. Any sulphur present in the extract may be determined by the method employed for the analysis of the pyridine extract in vulcanised rubber goods (page 303).

Before extracting the matter insoluble in epichlorhydrin with pyridine, the residue should be dried until free from the former solvent. The extraction with pyridine is then carried out as described on page 302, the flask being heated on a sand-bath or in an oil-bath. The pyridine is distilled from an oil-bath, and the residue dried until free from the odour of pyridine. The amount of sulphur in the extract, when required, may be determined as described on page 303.

The sulphur in the insoluble residue is next determined as in the case of total sulphur in rubber (page 313). The figure obtained gives the sulphur of vulcanisation and that present in the mineral matter.

The bases present in the mineral matter of the sample are determined and calculated as follows. Lead is calculated to PbO (litharge), antimony to the pentasulphide, and mercury to sulphide. Zinc may be present as oxide or sulphide; calcium as carbonate or sulphate; barium generally as sulphate, sometimes as carbonate; magnesium always as oxide. A little of the ebonite powder should be examined by heating with hydrochloric acid (1 : 3). Any hydrogen sulphide evolved will probably be due to zinc sulphide, and carbonic acid to calcium carbonate. The absence of barium from the solution obtained proves that any of this base present in the sample is in the form of sulphate. The sulphur thus found in inorganic combination is deducted from the sulphur in the insoluble residue F, when the percentage of sulphur of vulcanisation is obtained.[1]

The amount of rubber in the sample is obtained by difference.

Rubber Substitutes.

The manufacture of rubber substitutes (surrogates) has been the subject of innumerable patents. A large number of these so-called substitutes have as their basis, or starting-point, some one or other of the fatty oils, which are oxidised with the formation of solid products ("factis"). Other patents describe the preparation of substitutes for india-rubber from various compositions, containing such substances as leather, cork, asbestos, gelatin and glycerin, and ichthyol oil, with which are generally incorporated linseed oil and waste rubber. It is very doubtful whether these products have any real commercial value.

FATTY SUBSTITUTES (Oil Substitutes) for rubber are recognised in commerce in three varieties, namely, "white" and "brown" (black) substitutes, and "blown-oil" substitutes. They are generally yellowish elastic substances, with a slight penetrating odour and a moist and oily feel. They are insoluble in the usual solvents. "White substitute" is prepared by the action of sulphur mono-chloride (S_2Cl_2) upon the triglycerides of unsaturated fatty acids (linseed and colza oils) in the cold (100

[1] This method cannot be said to be invariably accurate, since zinc and barium may be present in two different forms, and error would thus result in the calculation. This is hardly likely to occur in the case of barium, according to C. O. Weber, but zinc may occur as oxide and as *lithopone* (page 312).

parts oil to about 25 parts of sulphur chloride), and "brown substitute" by the action of sulphur at high temperatures upon similar triglycerides, the oils being in the natural state or previously oxidised (blown). Thus white substitute is a chlorosulphide, and brown substitute a sulphide, of fatty oils. "Blown-oil substitutes" are prepared by the action of air or oxygen upon oils, and they consist therefore of oxides of triglycerides. Oil substitutes do not absorb any considerable amount of iodine, the sulphur chloride forming addition-products and converting the unsaturated fatty acids into saturated bodies (Henriques). Substitutes made from "blown" oils are known in the trade as "floating substitutes" (because, on account of their low specific gravity, they float on water). Substitutes made from ordinary oils are heavier than water.

R. Henriques (*J. S. C. I.*, 1894, page 48) has pointed out that since glycerides of the saturated fatty acids are indifferent to sulphur chloride, mixtures of these fats and of the ordinary oils would yield substitutes containing comparatively small amounts of sulphur chloride, and such substitutes would give analytical results very similar to those of substitutes prepared from oxidised cotton-seed oil. Boiling alcohol, however, would extract all the saturated fats from these compound substitutes, while the ordinary substitutes yield nothing to alcohol. Henriques states that saturated and unsaturated glycerides may possibly be separated by treatment with sulphur chloride, and subsequent extraction with alcohol.

These substitutes are not in any sense real substitutes for natural caoutchouc. Their true nature (that of fatty oils) is not changed by the vulcanisation treatment to which they have been subjected, as they are still triglycerides and therefore saponifiable. For this reason they cannot withstand many of the conditions to which manufactured rubber articles are subjected, such as high temperatures, steam, &c. These products are therefore simply organic filling-materials or adulterants, and their use is frequent because of the popular demand for cheap articles. Moreover, these substitutes are very liable to undergo spontaneous oxidation, which when begun may attack the true rubber in a mixture, with disastrous results.

The proportion of sulphur in the fatty substitutes is very variable, ranging from 5 to more than 17 per cent. The amount of soluble fatty oil and of free sulphur present should be small, since the presence of any considerable proportion of unaltered fatty oil causes deterioration of the rubber containing it, while when a large amount of free sulphur is present, it must be taken into consideration when the vulcanisation of the mixture of rubber and substitute is to be carried out, or over-vulcanisation

will be produced. White substitutes never contain more than traces of free sulphur, while oxidised oil substitutes contain neither sulphur nor chlorine. According to Weber, a white substitute should not contain more than 10 per cent. of soluble fatty matter and not less than about 8 per cent. of combined sulphur; while a brown (black) substitute should not contain more than 5 per cent. of soluble fatty matter, and the proportion of free sulphur should not exceed 40 per cent. of the amount of combined sulphur.

Similarity in chemical composition between samples of these substitutes does not necessarily imply equal suitability for mixing with india-rubber. The substitute added to rubber forms a solid emulsion with the latter, and the finer the emulsion formed, the better is the substitute. According to C. O. Weber, the examination of a thin film of the mixture of rubber and substitute under the microscope is the only reliable test. A solution of the consistency of thin honey is obtained by dissolving a small quantity of the mixture in benzene. A small drop of this solution is placed on the end of a microscope-slide, and another slide drawn rapidly across it. A thin quickly-drying film of the sample is thus obtained, and on examination under the microscope this should appear as an almost homogeneous mixture. Bad substitutes sometimes form no emulsion at all, but break up into a mass of streaky or scaly flakes.

"Brown" substitute is exclusively employed in those goods which are to be vulcanised by sulphur, whereas "white" substitute is generally used for cold-cured goods, *i. e.*, goods vulcanised by sulphur monochloride. Sometimes, as in the case of greyish-white gas-tubing, "white" substitute is used for sulphur-vulcanised rubber for the sake of the colour required, but the practice is detrimental to the quality of the finished article.

"Brown" substitutes, whether manufactured from natural or "blown" oils (in which latter case the oil is oxidised until it has a spec. gravity of about 0.960), are equally satisfactory, and the latter variety may be distinctly superior for certain purposes; but in the case of "white" substitutes those prepared from "blown" oils are not so good as the natural oil products, the former being somewhat unstable in character.

The following analyses of various fatty substitutes for india-rubber are given by R. Henriques (*J. S. C. I.*, 1894, page 47):—

	Commercial Products.					Linseed Oil Substitutes from		Colza Oil Substitutes from		Poppy-seed Oil Substitute, from Oxidised Oil.	Castor Oil Substitutes.		Substitute from Oxidised Cotton-seed Oil.
	White Substitute.			Brown Substitute.									
	A.[1]	B.[1]	C.[2]	A.	B.	Fresh Oil.	Oxidised Oil.	Fresh Oil.	Oxidised Oil.		With Minimum of S_2Cl_2.	With Maximum of S_2Cl_2.	
Sulphur,	6.4	6.17	8.25	15.48	17.71	9.34	4.78	8.28	6.59	7.68	4.82	10.6	6.23
Chlorine,	5.0	5.86	8.88	0.7	0.36	8.84	4.85	7.62	5.95	7.44	6.70	8.95	5.36
Water,	0.85	1.0	..	..	..	3.02	0.85	..	..	..	..	..	..
Mineral matter (Ash),	0.8	5.51	..	..	..	..	..	..	..	..	..	..	..
Fatty acids,	90.45	73.58	..	..	..	79.6	81.67	86.89	87.95	74.90	85.35	..	..
Sulphur in the fatty acids,	6.12	6.45	8.15	14.14	15.20	9.88	4.06	8.34	6.54	8.32	5.32	..	6.44
Chlorine in the fatty acids,	0.83	0.43	..	..	..	Trace	0.60	Trace	Trace	..	0.26	Trace	Trace
Iodine absorption of substitute,	30.9	31.0	32.6	42.0	42.0	56.3	52.6	32.5	26.9	33.6	35.2	21.9	30.3
Iodine absorption of fatty acids,	91.3	91.2	102.3	129.0	125.6	160.3	{141.2, 121.0}	101.5	102.8	133.3	{136.2, 147.4, 152.1}	143.5	91.5
Acetyl number,	..	..	..	..	..	21.0	19.6	31.0	..	..	..	105.6	51.3

[1] A and B, manufactured from oxidised oil. [2] C, from natural oil.

The foregoing results show the composition of these products as obtained from various oils. The methods for the determination of chlorine, &c., and for the identification of any particular substitute or mixture of substitutes in india-rubber, are given on pages 306, 314. The iodine absorption of the substitutes and of their fatty acids can be used for the determination of the nature of the oil present.

For the examination of the fatty substitutes as to their suitability for manufacturing purposes in admixture with india-rubber, the more important determinations are the free and combined sulphur, and the proportion of soluble fatty oil. Acetone is the best solvent to employ, and 3 to 5 grammes of the sample is extracted in a Soxhlet apparatus for four hours with this solvent. The acetone is evaporated from the extract, and the residue re-dissolved in acetone, when the fatty matters will quickly dissolve, leaving the sulphur in crystals, and almost insoluble. The liquid can be filtered to get rid of the fatty matters, and the free sulphur and fatty matters may then be weighed separately (see page 301).

The fatty matters extracted by acetone contain a certain portion of combined sulphur, so that if the amount of free sulphur found above be deducted from the total sulphur of the sample, the result is in excess of the truth, since only the sulphur combined in the insoluble substitute is reckoned as combined sulphur. The latter figure is therefore determined on the substitute after extraction with acetone. The same methods are employed as described under *India-rubber*.

The characters of the fatty acids obtained from a fatty substitute, or, in the case of rubber, isolated from the alcoholic soda extract, give a clue to the kind of substitute under examination. Thus the fatty acids from oxidised oil substitutes never contain more than traces of sulphur and chlorine, the substitute itself rarely containing sulphur or chlorine in amount exceeding 0.5 per cent. Brown (sulphide) substitutes contain usually from 4 to 9 per cent. of sulphur, the whole of which is found in the fatty acids when isolated. Only traces, at most, of chlorine are present in brown substitutes or their fatty acids. The fatty acids of white (chlorosulphide) substitutes contain the whole of the sulphur of the substitute, but the greater part of the chlorine is found in the alcoholic soda liquid on saponification. It may be determined in this alkaline solution as described on page 305.

In certain cases the kind of substitute or substitutes is only determined with difficulty. It has already been pointed out (page 305) that when a chlorosulphide substitute has been used in a hot vulcanised article, the greater portion of the chlorine is evolved as hydrochloric acid and combines

with the rubber of the sample, so that it is not found with the sulphur in the saponification liquors. In such a case, the substitute present may be erroneously regarded as a sulphide substitute. A determination of the sulphur and chlorine of vulcanisation (page 314) should next be made. If the rubber does not contain sufficient chlorine to be about equal to the sulphur in the alcoholic soda extract, the substitute present must be a sulphide (brown) substitute.[1] Cold vulcanised (sulphur chloride) goods never yield more than mere traces of free sulphur to acetone, while sulphide substitutes and hot vulcanised rnbber goods contain amounts of free sulphur which will readily be detected in the acetone extract.

"FENTON RUBBER" is manufactured (*Brit. Patent,* 1896, No. 26548) by mixing oxidisable vegetable oils, either in the natural or oxidised condition, with certain proportions of tar, pitch or creosote, and placing "the mixture, either cold or previously heated together, in a bath of diluted nitric acid, and allowing it to remain for maceration—cold, or quickening the reaction by boiling—until the whole is coagulated into a tough elastic magma having the appearance and nature of caoutchouc-like substance." The product is poured upon pans and roasted for a short time, when it coagulates into a highly elastic mass like rubber in appearance, and capable of being vulcanised. A similar process, without the addition of tar, &c., was first employed by Sachs and Jonas in 1848.

CALLENDER'S BITUMEN is much employed for large insulated electric cables. It is very similar to ordinary "brown substitute," and is manufactured by heating a mixture of stearin-pitch and sulphur under certain conditions.

"OXOLIN" is a patent substitute prepared by the oxidation of linseed oil, with which a vegetable fibre such as hemp is impregnated, the material being then spread on trays and repeatedly exposed to the air at a temperature of about 45°. It is then vulcanised by heating with sulphur in the ordinary way. In elasticity and tensile strength "oxolin" is much inferior to india-rubber. For certain purposes, however, this product may be used instead of the low brands of india-rubber.

W. F. Reid (*J. S. C. I.*, 1899, p. 972) has described a substance known as "VELVRIL" material, which is obtained by the addition of nitroricinolein (from castor oil) or nitrolinolein (from linseed oil), containing about 4 to 5 per cent. of nitrogen, to nitrocellulose of very low nitration. A homogeneous mass is thus produced, the substance obtained by using castor oil being preferable. The new substance is said to have given very good results,

[1] Only thin rubber surfaces are capable of being vulcanised by the cold process, so that when a rubber article of any thickness contains chlorine, it suggests the presence of a chlorosulphide substitute.

so far as elasticity and durability are concerned, and it is not more inflammable than india-rubber. "Velvril" material is insoluble in benzene, carbon disulphide and other solvents. At the temperature of boiling water, articles made with this material do not lose their shape, only becoming more supple. By greater heat and pressure, "velvril" can be moulded into any desired form. "Velvril" material seems likely to find use in a variety of ways, as, for instance, in the manufacture of belting, fabrics, insulating wire, hose and tubing, and as a cement and varnish, &c.

"RECOVERED" or "REGENERATED" rubber is usually manufactured from factory scraps and cuttings, or old rubber articles, such as goloshes and similar goods, which last-named materials almost invariably contain some asphaltum and lamp-black. In one form of recovery process, the material to be regenerated is treated with dilute sulphuric acid to separate or destroy the textile fabrics[1] present with the rubber, when the product is treated with steam under pressure.

Another method consists in heating the old rubber with a solution of calcium chloride, caustic soda, or other reagent, and grinding the rubber thus treated with mineral oil, and again heating the product.

The proportion of india-rubber in "recovered rubber" varies widely in different samples, from about 25 to (occasionally) 75 per cent., but usually not exceeding 35 to 40 per cent. Most samples of recovered rubber contain varying amounts of oils, rubber-substitutes, carbon, asphaltum, mineral matters, &c. Since, according to Weber, all recovered rubber contains 8 per cent. or upwards of mineral oils or even fatty oils, or a mixture of these, the recovery process also includes some method for the incorporation of these oils with the rubber. When recovered rubber is treated with a solvent capable of dissolving these oils, the rubber residue frequently assumes a condition very little

[1] Another kind of "recovered" rubber is that obtained from the cuttings of waterproof cloth vulcanised by the cold sulphur chloride process. After the removal of the textile materials, a rubber is obtained which is only properly vulcanised on the surface, the cold process leaving the under layers almost untouched. This rubber can be worked together by means of pressure between hot rollers. The rubber of course still contains chlorine, and can only be properly used again for "cold-cured" articles.

According to the process of C. J. Polôny (*J. S. C. I.*, *1903*, *page 752*) for the recovery of soft vulcanised rubber, the material in very small pieces is added to hot resin or amber oil (at 80° C.) containing about 5 to 8 per cent. of water. The mixture is then heated by steam under pressure, the temperature not exceeding 160° C. After one hour's boiling and several hours' standing, the rubber is contained in the top layer, which is mixed with pumice stone, gypsum, or other suitable material and the oil extracted by alcohol. The rubber in the residue is obtained by extraction with benzene, turpentine oil or ether. On evaporation the recovered rubber is obtained.

different from that of ground rubber-waste. Thus it will be seen that all recovered rubbers are dependent for their plasticity upon the solvent or softening action of these oils. Recovered rubber can therefore only find limited application, since products containing such oils are unsuitable for the manufacture of many classes of rubber goods. According to Weber, the best recovered rubber owes its great inferiority to native rubber to the fact that it undergoes further vulcanisation with the free sulphur present during the process of recovery (page 308). Rubber which has been more than once recovered contains greater proportions of combined sulphur according to the number of times it has gone through the recovery-process. The addition of "recovered" rubber to india-rubber does not appreciably alter the tensile-strength, but markedly affects the elongation according to the amount present.

The analysis of "recovered" rubber is carried out by the same methods as described under *Vulcanised Rubber*. The quantity and nature of the acetone extract[1] are useful data in judging of the value of samples of recovered rubber. Calculated upon the india-rubber of the sample, good recovered rubber should give an acetone extract below 10 per cent., although many commercial samples will be found to give at least 20 per cent. The smaller the amount of extract, the better the sample. The presence of saponifiable oils in the acetone extract should be ascertained by the Koettstorfer process. Weber suggests that, since the kind of fatty oil present is usually unknown, a mean saponification number of 190 be taken for the purpose of calculation, when the percentage of fatty oil is obtained by the formula:—

$$\frac{100 \times \text{KOH required in milligrammes.}}{190 \times \textit{grammes of acetone extract taken.}}$$

The saponification-number of the acetone extract should be only trifling, since the presence of fatty oils in india-rubber is liable to cause serious trouble.

The physical characters of the residue from the acetone extraction are important. Many commercial samples after extraction leave a residue consisting of a crumbly mass of rubber,

[1] C. O. Weber found a sample of recovered rubber to contain about 18 per cent. of an inferior kind of rubber known as Guayrule rubber, which was detected by means of its characteristic resin. Guayrule rubber is stated by C. Harries to yield a "nitrosite" identical with that from Para rubber, but the bromine-compound of the former contains only 45 per cent. of Br, while that from Para rubber contains 70 per cent. Weber concludes that Guayrule rubber contains a considerable quantity of oxygen, but P. Alexander (abst. *Analyst*, 1904, p. 334) states that the carefully purified products (Guayrule and Pontianac) showed only 2 per cent., at the most, of this constituent.

&c., which has practically no elasticity or plasticity. A good sample will leave an appreciably plastic residue. Recovered rubber which loses by extraction with acetone any valuable property it may have possessed is only useful as a "filling" material for mixing with india-rubber.

Henriques' cold nitrobenzene process (page 302) for the detection of asphaltum may be used in the analysis of recovered rubber after the acetone extraction has been made. Fatty substitutes are determined by Henriques' alcoholic soda process (page 303). To obtain an accurate determination of the sulphur of vulcanisation in a sample of recovered rubber, it is necessary to determine the sulphur in the resulting alcoholic soda solution. The same liquid should be tested for chlorine, which when present should always be determined.

Weber directs that the rubber left after the above extractions should be carefully dried (avoiding oxidation) and weighed out into two equal parts. The combined sulphur is determined in one of these, while the other portion is used for the hot nitrobenzene process or other method for the separation of rubber and mineral matter. The latter is then examined in the usual way, the presence or absence of carbon and vegetable or animal fibres being noted (page 310).

The presence of any appreciable amount of free sulphur in recovered rubber is evidence of the unsatisfactory nature of the recovery process employed. Since the aim of the recovery process is to de-vulcanise the rubber, any method at all likely to accomplish this object would first remove most of the free sulphur. On the other hand, the removal of all but small quantities of (free) sulphur does not necessarily imply that any de-vulcanisation has taken place.

When rubber has been subjected to a high temperature (say, 150°, or higher) during the process of recovery, it may be regarded as probable that the rubber itself will have been acted upon by the high temperature, and a certain amount of decomposition-products formed. Weber has suggested a method for the determination of such products in recovered rubber by isolating them as bromine-derivatives. These brominated decomposition-products (containing over 60 per cent. of Br) are insoluble in alcohol and very difficultly soluble in benzene, whereas the bromine derivatives of the oils present in recovered rubber are readily soluble in alcohol and benzene, and mixtures of these two solvents. For the purpose of determining these products, Weber dissolves the acetone extract (containing oils and decomposition-products of rubber) in sufficient of a mixture of two parts of benzene and one of absolute alcohol, and adds bromine in slight excess to the solution. The bromine compounds of any decomposition-products present are precipitated,

and can be filtered off. The precipitate is washed first with the mixed solvents and finally with alcohol, and then dried at 50°. Weber found that in eight samples of recovered rubber the percentage of bromine in the compound obtained varied from 62.5 to 67.1, so that it is necessary to determine the bromine in the compound obtained and subtract the weight found from the total weight of the precipitate. The percentage of decomposition-product can then be calculated. Three recovered rubbers examined by Weber, and which had been prepared from the same rubber scrap with mineral oil at temperatures of 140°, 160°, and 185°, gave respectively the following percentages of decomposition-products: 1.16; 1.86; 2.53 per cent. The process is likely to prove useful when the cause of the deterioration of any sample of manufactured india-rubber is to be investigated.

OLEFINIC TERPENE ALCOHOLS AND ALDEHYDES.

In addition to the oxygenated derivatives of the terpenes and their allies, and substituted phenols of which thymol and eugenol are types, there exist in various essential oils certain open-chain alcohols containing ten atoms of carbon which, with their associated aldehydes, are of considerable interest and practical importance. The following are the principal members of the group:—

Alcohol.			Aldehyde.		
Name.	Formula.	Chief Sources.	Name.	Formula.	Chief Sources.
Geraniol, . . .	$C_{10}H_{17}.OH$	True geranium and palmarosa oils. Rose oil, citronella oil &c.	Citral or Geranial.	$C_9H_{15}.COH$	Oils of lemon-grass, citronella, &c.
Linalol, ...	$C_{10}H_{17}.OH$	Oils of linaloe, bergamot, neroli, lavender, &c.			
Citronellol, .	$C_{10}H_{19}.OH$	African geranium oil, citronella oil, rose oil, &c.	Citronellal,	$C_9H_{17}.COH$	Oil of citronella, *Eucalyptus maculata*, &c.

The bodies which have been described under the names of rhodinol, lavendol, licareol, coriandrol, nerolol, aurantiol, &c., appear to be all more or less pure geraniol or linalol. Roseol from Bulgarian rose oil is merely impure citronellol. *Menthocitronellol*, a body obtained by a series of reactions from menthone, $C_{10}H_{18}O$, is identical or isomeric with citronellol. Nerol, isomeric with geraniol and present in oils of neroli and petitgrain; and

farnesol, present in cassie-flower oil and possibly in otto of rose, are probably true chemical individuals.

F. W. Semmler (*Ber.*, xxiv, 201) applies the term "olefinic camphenes" to the bodies formulated above, and points out that such open-chain compounds have a specific gravity of 0.86 to 0.90 at 20°/20°, and a higher refractive index than the isomeric compounds with closed chains.

GERANIOL. $C_{10}H_{17}.OH$

Geraniol is a monatomic primary open-chain alcohol isomeric with linalol, which is a tertiary alcohol (page 330). The following formulæ probably express their constitution:—

GERANIOL. $(CH_3)_2C{:}CH.CH_2.CH_2.C(CH_3){:}CH.CH_2OH.$
LINALOL. $(CH_3)_2C{:}CH.CH_2.CH_2.C(CH_3)OH.CH{:}CH_2.$

Geraniol is the principal constituent of true geranium oil, and of the oil of palmarosa, or so-called "Turkish geranium." It is also one of the chief fluid constituents of rose oil, and is present to a considerable extent in citronella oil and in smaller proportions in the oils of lavender, lemongrass, *Eucalyptus maculata*, &c.

Geraniol may be isolated from oils containing not less than 25 per cent. by converting it into its crystalline compound with calcium chloride, $(C_{10}H_{18}O)_2,CaCl_2$.[1]

Geraniol may be prepared on a commercial scale (*German Patent*, No. 80,007) by distilling geranium or pelargonium oil under reduced pressure (14 mm.), and heating the fraction which distils between 120° and 130° in an autoclave with acetic anhydride. The resulting esters are fractionated, distilled, the fraction passing over between 127° and 132° (consisting chiefly of geranyl acetate) saponified with alkali, and the liberated geraniol fractionated *in vacuo*. The portion distilling between 120° and 125° consists essentially of geraniol and forms the "rhodinol" of commerce.

As prepared by the foregoing methods, geraniol always contains more or less citronellol, from which it may be separated by converting it into acid geranyl phthalate in the manner prescribed by Flatau and Labbé (page 333).

Lemon-grass oil contains from 4 to 6 per cent. of free geraniol, and a further proportion in the form of esters. Schimmel & Co.

[1] For the production of this body, the oil, previously dried by anhydrous sodium sulphate, is intimately mixed in a mortar with an equal weight of recently-fused calcium chloride. The mixture is kept under a desiccator for twenty-four hours, at or below 0° C., and is then triturated with dry ether or petroleum-ether. The liquid portion is separated by a suction filter and the crystalline mass treated with water, when the compound is decomposed and the liberated geraniol separates as an oily layer. This is separated and redistilled under reduced pressure.

have systematically manufactured geraniol from this source, using for the purpose the residues resulting from the preparation of citral by the bisulphite process.[1]

Geraniol may be prepared from citral (geranic aldehyde) by treating an alcoholic solution of that substance, feebly acidulated with acetic acid, with sodium-amalgam. To obtain a pure product, the solution should be heated with alkali to decompose unaltered citral, and steam-distilled, rejecting the last portions of the distillate.

Geraniol is a colourless, highly-refractive liquid, having a fragrant rose-like odour, and a specific gravity of 0.882 to 0.885 at 15° C. It boils at 230° at the ordinary pressure, and at 120° under a pressure of 16 mm., and is optically inactive. Geraniol is not sensibly soluble in water, but dissolves with facility in strong spirit, and forms a clear solution with from twelve to fifteen volumes of 50 per cent. alcohol.

On exposure to air, geraniol very readily undergoes oxidation, with production of its aldehyde *geranial* or *citral*, $C_{10}H_{16}O$, the specific gravity and boiling-point of the liquid increasing.

On treatment with chromic acid mixture, geraniol is converted into *citral* or *geranial*, and on oxidation with permanganate it yields *iso-valeric acid*. Dehydrating agents convert geraniol into inactive *terpenes* (cinene and terpinene).

By heating with acid anhydrides, geraniol is readily converted into the corresponding *esters*. Conversion into geranyl benzoate and acid phthalate is used for the purification of geraniol.[2] *Geranyl acetate*, $C_{10}H_{17}.C_2H_3O_2$, occurs naturally in certain essential oils. It is a colourless liquid having a powerful aromatic odour, and is much valued in perfumery. The specific gravity is 0.9174, and the boiling-point 128° to 129°, under a pressure of 16 mm.

F. Tiemann (*Ber.*, 1898, xxxi, 2989) states that when geraniol is heated with very strong alcoholic potash to 150° for eight

[1] In order to ascertain that the geraniol pre-existed in the oil, and was not a product of the reducing action of sodium bisulphite on citral, Schimmel & Co. employed the following method: Lemon-grass oil was heated for some time on a water-bath with benzoic anhydride, the citral and other volatile matters removed by steam-distillation, and the residue boiled with alcoholic alkali to decompose the geranyl benzoate. The alcohol was removed by evaporation, the residue redistilled with steam, the oily portion of the distillate treated with calcium chloride, and the resultant compound of geraniol purified and decomposed by water. The geraniol thus obtained was optically inactive, boiled at 229° to 230°, had a specific gravity of 0.8808 at 15°, a refractive index of 1.47665 at 17°, and reacted with diphenyl carbamine chloride to form a *diphenyl-urethane* melting at 82°.

[2] Treatment with phthalic anhydride affords a sharp distinction between geraniol and linalol, the former being converted into an acid phthalate while the latter is unattacked.

hours, it is hydrolysed with formation of ethyl alcohol and *methyl-heptenol*, $(CH_3)_2C:CH.(CH_2)_2.CO.CH_3$.[1] This compound boils at 85° to 86° under a pressure of 15 mm., and at 175° to 176° at the ordinary atmospheric pressure. Linalol remains almost unchanged when heated with strong alcoholic potash.

According to H. and E. Erdmann (*Jour. prakt. Chem.*, 1897, lvi, 1), if 1 drop of geraniol ("rhodinol") be diluted with 5 cc. of alcohol, and 10 drops of strong sulphuric acid added without shaking, the acid sinks and takes an intense orange-yellow colour, while on gently moving the vessel the colour turns to reddish-violet at the surface of junction of the two liquids. Linalol shows a similar reaction, but the colour is less stable and readily changes to brown. Citronellol gives a feebler coloration of a bluish tint.

H. and E. Erdmann (*Jour. prakt. Chem.*, liii, 42; lvi, 1, 27) have also described a method of detecting geraniol based on the formation of its diphenyl-carbamate (geraniol-diphenyl-urethane).

Commercial Geraniol. ***Rhodinol.*** Eckart originally described the mixture of liquid alcohols from rose oil by the name of *rhodinol*, but it is now admitted that these and similar products consist essentially of geraniol with more or less citronellol, which, if not separated by special means is always present in commercial geraniol.[2] The name rhodinol is now applied to the product from geranium oil and other sources.

By the action of dilute acids, many of the derivatives of geraniol are converted into cyclic isomerides of the same molecular weights, but having lower boiling-points, higher specific gravities, and somewhat lower indices of refraction than the open-chain compounds from which they are derived.

Linalol. (Linalool.) $C_{10}H_{17}.OH$

Linalol is a monatomic open-chain alcohol, isomeric with geraniol (page 328), from which it differs in being optically active. Linalol is the essential constituent of oil of linaloe, and also exists, in the free state or in the form of esters, in the oils of petitgrain, bergamot, coriander, lavender, neroli, *Asarum Canadense*, &c.

Two isomeric forms of linalol exist, and these are often co-existent in natural essential oils. Hence natural linalol differs

[1] According to P. Barbier, *dimethyl-heptenol* is the product of the reaction.

[2] Varieties of geraniol also result from the practice of distilling the liquid over different flowers, to obtain products described as rose-geraniol, mignonette-geraniol, &c., some of which are greatly preferable as perfumes to ordinary geraniol.

in optical activity, and has been described, according to its origin, under the names of *aurantiol*, *coriandrol*, *lavendol*, *licareol*, *nerolol*, &c. The purest form of dextro-linalol is obtained from coriander oil, while the purest form of lævo-linalol is that known as licareol. The physical properties of these two modifications are compared in the following table by F. Tiemann (*Ber.*, 1898, xxxi, 806):—

	CORIANDROL. (*d*-linalol.)	LICAREOL. (*l*-linalol.)
Boiling-point under reduced pressure,	86°–87° at 14 mm.	85°–86° at 12 mm.
Specific gravity,	0.8622 at 20°	0.8726 at 17.5°
Refractive Index for the D line,	1.46108	1.46455
Molecular Refraction,	49.13	48.78
Angular Rotation, in 1-decimetre tube,	+16°.92	—11°.60
$[\alpha]_D$,	+19°.62	—13°.32

Linalol is a colourless or nearly colourless liquid, having an odour suggestive at once of roses and lemons. It boils, under the ordinary pressure, at 197° to 198°.

Linalol is employed in perfumery, as is also *linalyl acetate*, $C_{10}H_{17}.C_2H_3O_2$, which is a liquid smelling powerfully of bergamot, in the oil of which it exists naturally in considerable proportion (40 per cent.). Linalyl acetate is also a constituent of the oils of lavender and petitgrain. This ester is stated by H. E. Burgess to give a permanent brilliant violet coloration when shaken with about three times its measure of a 10 per cent. mercuric sulphate solution in 25 per cent. sulphuric acid.

By treatment with hydrochloric acid, linalol yields a liquid *chloride* containing $C_{10}H_{18}Cl_2$, which has an odour like that of camphor and by distillation with lime yields a *terpene* of characteristic odour boiling at 168° to 172° C. Linalol combines with four atoms of bromine.

By treating linalol with acetic anhydride, and saponifying the linalyl acetate formed, Barbier obtained a product which he named licarhodol. K. Stephan (*Jour. prakt. Chem.*, lviii, 109) states that a strongly dextro-rotatory, crystalline terpineol is formed under these conditions, and that Barbier's product was probably a mixture of this terpineol with linalol and geraniol. Stephan states that acetic acid does not act on linalol till the mixture is warmed, whereas concentrated formic acid readily converts lævo-linalol into dextro-terpineol, and dextro-linalol (coriandrol) into lævo-terpineol.

According to H. E. Burgess (*Analyst*, 1900, page 265), linalol gives an immediate deep violet coloration when shaken with two or three times the quantity of a 10 per cent. solution of mercuric sulphate in 25 per cent. sulphuric acid.

CITRONELLOL. $C_{10}H_{19}.OH$

Citronellol is an open-chain alcohol closely related to geraniol, from which it differs in formula by two atoms of hydrogen.[1] It occurs in association with geraniol in rose oil, geranium oil, &c., and is also obtainable by the reduction of its aldehyde, citronellal,[2] which occurs in oil of citronella, &c.

Citronellol is a fragrant oily liquid, of 0.8565 specific gravity at 17.5°, and a refractive index of 1.4566. It boils at 117° to 118°, under a pressure of 17 mm., and at the ordinary pressure, with some decomposition, at 225° to 230° C.

Citronellol obtained by the reduction of citronellal exhibits a dextro-rotation of about $[a]_D = +4°$, whereas the variety isolated from rose oil is lævo-rotatory. In many specimens of geranium oil both varieties coexist. Both optical isomerides of citronellol yield *p*-methyl-adipic acid when oxidised with chromic acid mixture, and the product exhibits optical activity of the same kind as the alcohol from which it was derived.

Citronellyl Acetate, $C_{10}H_{19}.C_2H_3O_2$, is a fragrant oily liquid, of 0.8928 specific gravity at 17.5°. It boils at 120°, under a pressure of 15 mm. and exhibits dextro-rotation ($[a]_D = +2.4°$).

DETERMINATION OF OPEN-CHAIN ALCOHOLS IN ESSENTIAL OILS.

The determination of the total alcohols present in essential oils may be effected by converting them into their acetic esters (by treatment with acetic anhydride) and ascertaining the amount of alkali required for the saponification of the esters formed. The process, which is described in detail on page 230, is vitiated by the presence of any notable amount of citronellal, which is readily converted into isopulegyl acetate and thus renders the result too high. From oils containing them, the aldehydes should first be removed by treatment with sodium bisulphite solution, the alcohols and other non-aldehydic constituents extracted with ether, and the residue left on evaporation of the ether employed for acetylisation.

The accurate separation of the open-chain alcohols from each

[1] According to Tiemann and Schmidt, the constitution of citronellol is represented by the formula:—

$$(CH_3)_2.C:CH.CH_2.CH_2.CH(CH_3).CH_2.CH_2.OH,$$

but Barbier, Bouveault and others represent it as:—

$$CH_2:C(CH_3).CH_2.CH_2.CH_2.CH(CH_3).CH_2.CH_2OH.$$

[2] Citronellol is not obtainable by the direct action of nascent hydrogen on geraniol. If, however, a solution of geranic acid in boiling amylic alcohol be treated with sodium, citronellic acid is obtained, and when a mixture of calcium citronellate and formate is subjected to dry distillation citronellal is formed, which can be reduced to citronellol by treatment in alcoholic solution with sodium-amalgam. The compounds obtained by the foregoing processes are optically inactive.

other is attended with difficulty, and cannot in all cases be satisfactorily performed. The separation of geraniol and citronellol may be approximately effected by the following method of Flatau and Labbé (*Compt. rend.*, cxxii, 1725):—The oil is saponified with alcoholic potash, and rectified *in vacuo*. The portion distilling between 120° and 140° C. at 30 mm. pressure is dissolved, together with an equal weight of phthalic anhydride, in an equal volume of pure benzene. After boiling the mixture for an hour under a reflux-condenser the benzene is evaporated off, and the residue treated with caustic soda. The gelatinous mass thus obtained is dissolved in tepid water, and the solution shaken with ether to remove impurities. The esters are then liberated by adding hydrochloric acid diluted with an equal measure of water, and washed out with petroleum-ether at about 25° C. The petroleum solution is then cooled to —5° C., when the *acid geranyl phthalate* separates out completely (in the course of a week!) in well-formed crystals.[1] On removing these and evaporating the mother-liquor, the *acid citronellyl phthalate* is left as a yellow oily residue which does not crystallise on cooling. The two esters thus obtained are then saponified separately with 5 per cent. alcoholic potash, and the liberated alcohols purified by redistillation in a current of steam.

By the above process, Flatau and Labbé obtained the following percentages of open-chain alcohols from typical oils containing them:—

Kind of Oil.	Total Alcohols.	Geraniol.	Citronellol.	Linalol.
Indian Geranium, ...	80	63	17	..
African (Bourbon) Geranium, ...	80	10	70	..
Melissa, ...	32	20	..	12
Bulgarian Rose, ...	85 to 90	70	15	..
Citronella, ...	46	40	6	..

Schimmel & Co. state that the foregoing method is well suited for the preparation of pure geraniol, since the crystals readily separate and the alcohol obtained is as pure as that prepared by the calcium chloride method. On the other hand, the citronellol is always impure, owing to geranyl phthalate being not

[1] Geranyl phthalate crystallises in shining rhombic tablets which melt at 47°, and are readily soluble in the usual solvents in the cold, and in petroleum spirit at 25°. It begins to separate on cooling its solution in petroleum spirit to about 10°, and is almost insoluble at —5° C. Silver geranyl-phthalate is a white powder melting at 133.8° C. (?138.8). By treating geranyl-phthalate dissolved in ether with bromine, a tetrabromoderivative is obtained melting at 114° to 115°. These compounds may be employed for the identification of geraniol.

wholly insoluble in petroleum-ether. Hence the method is not suited for the quantitative determination of the two alcohols in essential oils. To the inaccuracy of the method Schimmel & Co. attribute the detection of 17 per cent. of citronellol in palmarosa oil, a product which they assert contains mere traces, if any, of that body.

According to Tiemann and Schmidt (*Ber.*, xxix, 903), the following method of detecting and determining citronellol in admixture with geraniol gives very satisfactory results:—

A solution of 100 parts of the sample under examination in 100 parts of absolute ether is cooled and added very gradually to a solution (cooled to —10° C.) of 60 parts of phosphorus trichloride in 100 parts of ether. During this operation the temperature must not be allowed to rise above 0° C. The mixture is allowed to stand for four or five days at the ordinary temperature, and is then poured out on crushed ice, the ethereal layer washed several times with ice-water and agitated vigorously with dilute caustic soda solution, which extracts from it *citronellol (in the form of a chlorinated phosphorus ester-acid)*, leaving behind geranyl chloride, &c. The soda solution is shaken once or twice with ether to remove impurities, rendered strongly alkaline, and steam-distilled in order to separate the liberated citronellol. The yield of citronellol is quantitative from samples containing not less than 20 per cent. of geraniol. Dextro-citronellol may be readily prepared in this way from citronella oil, which is first treated with sodium-amalgam in order to reduce the citronellal present, and the above process directly applied to the resulting mixture of alcohols.

The following figures are given by Tiemann and Schmidt as illustrating the application of the process to different oils:—

	Percentage of Total Alcohols.	Per 100 parts Total Alcohols.	
		Geraniol.	Citronellol.
Turkish Rose oil, ...	80	75	(*l*—) 25
Spanish Geranium oil, ...	70	65	(*l* and *d*) 35
African Geranium oil, ...	75	80	(*d* and *l*) 20
Réunion Geranium oil, ...	80	50	(*d* and *l*) 50

The citronellol from Réunion oil apparently contained traces of linalol. The so-called *réuniol* obtained by Hesse from the same source was found to be a mixture of geraniol with dextro- and lævo-citronellols, the latter modification predominating.

The method of acetylisation, which is applicable to the determination of the alcohol geraniol in a large number of oils,

fails in the case of oil of citronella, since the isomeric body citronellal, present therein in considerable proportion, is by treatment with acetic anhydride converted quantitatively into the acetic ester of isopulegol. Hence the result will be a measure of the geraniol of the oil *plus* the citronellal present. Till recently, the figure so obtained was taken as the criterion of value of citronella oil, but Schimmel & Co. (*Report*, Oct., 1899) have proposed a method by which the actual geraniol present can be determined, while the difference between the amount found and the result of the acetylisation process gives the citronellal of the sample. Schimmel's method is based on the conversion of the geraniol into its acid phthalate by treatment with phthalic anhydride, which has no action on citronellal. Secondary alcohols, like borneol, are scarcely attacked; while tertiary alcohols, such as linalol and terpineol, are wholly unacted on. Schimmel & Co. recommend that to 2 grammes of the oil under examination about 2 grammes of phthalic anhydride should be added, together with 2 cc. of benzene, and the mixture heated on a water-bath for two hours in a flask furnished with a reflux-condenser. After cooling, the mixture is shaken for ten minutes with 60 cc. of carefully-measured seminormal caustic alkali solution, the flask being kept closed by a glass stopper. By this treatment the excess of phthalic anhydride is converted into potassium (or sodium) phthalate, and the acid geranyl phthalate into a neutral compound. The excess of alkali is then titrated back with seminormal sulphuric acid. The difference between the volume of standard acid required and that of the alkali originally employed is equivalent to the phthalic anhydride which has reacted with the geraniol. Thus 1 cc. deficiency of normal alkali represents 0.148 gramme of phthalic anhydride ($C_8H_4O_3$), or 0.154 gramme of geraniol ($C_{10}H_{18}O$).

CITRAL. GERANIAL. $C_9H_{15}.COH$; or,

$$(CH_3)_2C:CH.CH_2.CH_2.C(CH_3):CH.COH$$

This body is the aldehyde of geraniol (page 328). It has the same centesimal composition as camphor, but differs from that substance greatly, being an open-chain compound.

Citral occurs largely in the oil of lemon-grass (*Andropogon citratus*) and in various other essential oils.[1] It also results from the oxidation of geraniol and linalol.

[1] Lemon-grass oil contains from 75 to 85 per cent. of citral, which also occurs in the oils from the rinds of the fruits of the lemon, citron, lime, mandarin and citronella. It is likewise present in the oils from Japan pepper (*Xanthoxylum piperitum*), *Eucalyptus Staigeriana*, and *Backhausia citriodora*, the last mentioned yielding an oil containing 95 per cent. citral. Citral is contained in small quantities in bay and orange oils, and is probably present in melissa oil.

Citral is a golden-yellow liquid having the fragrant odour of oil of lemon, which contains about 3 to 4 per cent. of this aldehyde (see page 432). It has a specific gravity of 0.895 at 15° C.,[1] boils at 228°, and when pure is optically inactive.

Citral easily undergoes change on exposure to air and light and is acted on readily both by acids and alkalies. By treatment with the latter it is resinified with formation of substances which volatilise with difficulty (? polymers). Alkalies simultaneously exercise a hydrolysing action on citral, forming *methylheptenone*, $C_8H_{14}O$ (page 366), and acetaldehyde, C_2H_4O, so that the reaction is very complex.

According to F. Tiemann (*Ber.*, 1899, p. 115; 1900, pp. 3703, 3710), two stereo-isomers of citral exist. These have the same physical properties, but yield semicarbazones melting respectively at 164° and 171°; the isomer yielding the former semicarbazone largely predominating both in natural citral and that obtained by the oxidation of geraniol or linalol. Both varieties of citral behave in the same manner with bisulphites (page 340), and give the same products on oxidation and on decomposition by potash.

Citral behaves similarly to citronellal (page 337) when treated with molecular proportions of pyroracemic acid and *b*-naphthylamine.[2] The citral-β-naphthocinchoninic acid obtained forms lemon-yellow laminæ melting at 197°.

By treatment with hydriodic acid or acid potassium sulphate citral is converted quantitatively into *cymene*, $C_{10}H_{14}$. This reaction confirms the constitutional formula already given.

When treated with silver oxide and ammonia, citral is converted into the corresponding acid, *geranic acid*, $C_{10}H_{16}O_2$.[3]

[1] This is the gravity of the citral now manufactured by Schimmel & Co.

[2] F. Tiemann has pointed out (*Ber.*, 1898, xxxi, 3324) that if the citral is not present in theoretical proportion, the pyruvic or pyroracemic acid is partially decomposed, and α-methyl-β-cinchoninic acid is formed, melting at 210°. *In addition, a neutral substance is produced, which can only* be separated by repeatedly dissolving the acid in ammonia, and reprecipitating it by acetic acid. Pure citral gives about 45 per cent. of the theoretical yield (or nearly its own weight) of citryl-β-naphtho-cinchoninic acid. If Doebner's reaction be applied to a mixture of citral and citronellal the citryl compound crystallises out first, and citronellyl-β-naphthocinchoninic acid, melting at 225°, can be obtained from the mother-liquor. Tiemann states that 10 per cent. of citronellal in citral can be detected with certainty in this manner.

[3] *Geranic Acid*, $C_9H_{15}C.OOH$, is prepared more readily by the action of alcoholic potash on geranionitrile. It is an oil having an odour like that of the higher fatty acids. By the action of somewhat diluted sulphuric acid (*e. g.*, 65 per cent.), it is converted into iso-geranic acid, a cyclic compound of the same molecular weight. By rapidly adding metallic sodium to a boiling solution of an equal weight of geranic acid in amylic alcohol, *citronellic acid*, $C_{10}H_{18}O_2$, is formed, identical with that obtained from citronellal through the oxime and nitrile.

CITRONELLAL. Citronellic Aldehyde. $C_9H_{17}.COH$

Citronellal occurs in large proportion (10 to 20 per cent.) in oil of citronella, and in certain kinds of geranium oil. It is also present in the oil of *Eucalyptus maculata* (var. *citriodora*), and in very small proportion in lemon and lemon-grass oils.

Citronellal is a colourless oily liquid, of agreeable citronella-like odour. It is optically active ($[\alpha]_D = +8.18°$),[1] has a specific gravity of 0.8768 at 17.5° C., and a refractive index of 1.4481. It boils and distils with slight decomposition between 205° and 208°. E. J. Parry found the purest commercial substance to have a spec. gravity of 0.873, and to be only slightly optically active.

By the action of reducing agents (sodium amalgam), citronellal is converted into the corresponding alcohol, *citronellol*, $C_{10}H_{19}.OH$.

When heated with acetic anhydride, citronellal is converted into the isomeric cyclic alcohol, *isopulegol*,[2] closely resembling pulegol. This and other reactions justify the following constitutional formula for citronellal:—

$C(CH_3)_2{:}CH.CH_2.CH_2.CH(CH_3).CH_2.COH$. The formula

$CH_2{:}C(CH_3).CH_2.CH_2.CH_2.CH(CH_3).CH_2.COH$

is preferred by Harries and Schauweeker (*Ber.*, 1901, p. 2981).

Labbé states (*Ber.*, 1899, xxxii, 3338) that pure citronellal is apt to undergo complete and rapid isomerisation into *iso-pulegol*.

Citronellal was formerly regarded as a ketone, and hence was designated *citronellone*, but its aldehydic constitution appears to be established by a reaction observed by O. Doebner (*Ber.*, 1894, xxvii, 352), which depends on the formation of *citronellyl-β-naphthocinchoninic acid*. This compound is prepared by treating citronellal (more than one molecule), dissolved in absolute alcohol, with a solution of one molecule of pyroracemic (pyruvic) acid in the same menstruum, and adding a solution of one molecule of β-naphthylamine in absolute alcohol. The mixture is heated on a water-bath for three hours and then

[1] According to Tiemann and Schmidt (*Ber.*, xxix, 903), citronellal exists in two optically-opposed modifications, which on oxidation with chromic acid mixture yield the corresponding dextro- and lævo-*β-methyl-adipic acids*, $(CO.OH)CH_2.CH_2.CH(CH_3).CH_2.CO.OH$. Acetone is simultaneously formed.

[2] Commercial citronellal is a colourless, slightly dextro-rotatory liquid of about 0.873 specific gravity. On treatment with sodium bisulphite and carbon dioxide (page 341) it leaves about 6 per cent. of residue smelling of isopulegol (peppermint-like odour) and containing alcohols (probably geraniol and citronellol) in small quantity. On oxidation with chromic acid mixture this residue yields *iso-pulegone* (F. Tiemann, *Ber.*, 1899, p. 825).

allowed to cool, when the acid crystallises out in colourless needles melting at 225° C. Doebner recommends the reaction for the detection and determination of citronellal in essential oils.

Citronellal reacts violently with free sulphurous acid, terpenes and other products being formed, and a similar reaction takes place with sodium bisulphite containing free acid. The normal bisulphite-compound, $C_9H_{17}.COH,NaHSO_3$, is best prepared by treating the aldehyde with an ice-cold solution of neutral sodium sulphite to which the calculated quantity of acetic acid has been added. So prepared, and purified by kneading with alcohol and washing with ether, the compound is quite stable. It is quantitatively decomposed by sodium hydroxide or carbonate at the ordinary temperature. By the action of bisulphite solution containing sulphite on citronellal or its normal bisulphite-compound, a body is formed of the formula:—$C_9H_{18}(SO_3Na).CH(OH).SO_3Na$. By the action of sodium carbonate this is converted into the *hydrosulphonate*, $C_9H_{18}(SO_3Na).CHO$, from which caustic soda does not liberate citronellal, even on boiling.

On treatment with hydroxylamine, citronellal yields an *oxime*, $C_{10}H_{18}.NOH$, as an oil of 0.906 specific gravity, boiling at 135° at 14 mm. pressure.

H. E. Burgess has observed (*Analyst*, 1900, page 265) that citronellal gives a bright yellow colour, which is fairly permanent, when a little of the aldehyde is shaken with two or three times the quantity of a 10 per cent. solution of mercuric sulphate in diluted sulphuric acid (25 per cent.). Citral gives a bright red evanescent coloration.

Determination of Citral and Citronellal.

The determination of citral in essential oils is attended with peculiar difficulties.[1] Theoretically it should be possible to reduce the aldehyde to geraniol, which could then be acetylated and saponified, and a process on these lines has been described by H. Garnett (*Pharm. Jour.*, lvi, 321), but the alteration cannot be relied on to take place quantitatively in one particular manner. Every reaction is accompanied by the formation of bye-products of resinification, such as methyl-heptenone, acetone, cymene, &c. This is the case even when the reduction of the citral to geraniol is conducted in alcoholic solution. The usual process based on the production of the bisulphite compound of citral is also open to exception, owing to the unavoidable formation of soluble sulphonic compounds.[2] Hence the method may

[1] Except in cases such as that of lemon-grass oil, which contains a large proportion of this aldehyde.

[2] In the process of Tiemann, described on page 341, advantage is taken of this tendency and an apparently accurate method based thereon.

be useful for ascertaining the comparative value of commercial samples of oils containing citral, but not for the accurate determination of the proportion of aldehydes present.

The condensation-product of citral with cyanacetic acid has been obtained by F. Tiemann (*Ber.*, xxxi, 3329) as a readily-crystallisable compound, well adapted for the detection and determination of citral in essential oils. A solution of cyanacetic acid in three parts of water is mixed with two equivalent proportions of caustic soda (in the form of a 30 per cent. solution), and one equivalent proportion of citral then shaken with the alkaline liquid. Pure citral dissolves completely, and on acidifying the liquid, the citralidene-cyanacetic acid separates as an oil which soon becomes crystalline. The product, which is from 92 to 95 per cent. of the theoretical, is re-crystallised from warm benzene, or from a mixture of benzene and petroleum spirit, when a yield of 73 to 75 per cent. of the theoretical is obtained, the resulting yellow crystals melting at 122° C., and having the composition $C_9H_{15}.CH:C(CN)COOH$. The citral in essential oils may be determined by shaking the oil with an alkaline solution of the cyanacetic acid. After repeatedly shaking out the alkaline liquid with ether, the citral compound is liberated by acidifying the liquid.

E. J. Parry first concentrates the oil to be examined for citral (lemon oil) by distilling off about 85 per cent. of the terpene at a pressure of 12 to 13 mm. The distillate contains only the merest traces of citral. Two hundred cc. of the oil thus yields about 25 cc. of concentrated residue, the specific gravity of which is first determined. Ten cc. of the liquid is then shaken with a solution of about 5 grammes of cyanacetic acid and an equal weight of caustic soda in 30 cc. of water, the operation being performed in a small absorption-flask having a long, graduated neck. The unabsorbed portion of the oil is measured,[1] and the percentage of citral thus obtained, after correcting for the specific gravity of citral (0.897). The specific gravity of citral is so near to that of the concentrated oil that they may be taken as identical. Parry states that the method has given fairly accurate results in his hands and the value of the method has been confirmed by Schimmel & Co. The cyanacetic acid must, however, be quite fresh, as there is reason to believe that it changes on keeping and then gives erratic results.

F. Tiemann (*Ber.*, 1898, xxxi, 3297); *J. S. C. I.*, xviii, 169) has shown that the reaction of citral with alkali-metal sulphites

[1] A little trouble in measurement sometimes occurs, owing to the stearoptene of the oil forming a layer on the surface of the liquid, but in Parry's opinion the difficulty is trifling. It may be wholly overcome by steam-distilling the citral from the concentrated residue, and operating on the steam-distillate.

varies with the conditions of the experiment. Thus on agitating 100 parts of citral with 100 of sodium bisulphite dissolved in 200 parts of water and 25 parts of glacial acetic acid, the normal bisulphite compound, $C_9H_{15}.CHO,NaHSO_3$, is formed quantitatively. Partial dissociation occurs on dissolving the compound in warm water, and on regenerating the citral a loss of from 10 to 15 per cent. always occurs from a partial conversion of the normal compound into a hydrosulphonic acid derivative. A stable dihydrosulphonate, $C_9H_{17}(SO_3Na)_2.CHO$, not decomposed by alkali-metal carbonates or hydroxides, is obtained by the action of excess of bisulphite solution (which must be maintained acid throughout) on the double sulphite compound. An unstable dihydrosulphonate of the same formula as the above is obtained by the action of a slightly alkaline solution of sodium sulphite on citral or its normal bisulphite compound. For its formation, Tiemann recommends that 100 parts of citral should be shaken with 350 parts of sodium sulphite, Na_2SO_3, 7aq, and 125 parts of sodium bicarbonate for several hours. The product is then extracted with ether to remove non-aldehydic impurities, and the citral liberated by caustic soda. The solution of alkali should be previously saturated with ether, a layer of ether poured on the aqueous solution, and the soda added gradually, so as to expose the citral to its action for as short a time as possible. Tiemann recommends this process for the determination of citral in lemon-grass oil. Under the prescribed conditions, geraniol and linalol do not form hydrosnlphonates, while citronellal is converted into sodium citronellylhydrosulphonate, which is not decomposed by caustic soda, even on boiling.

Tiemann gives the following results of determinations of citral in a sample of lemon-grass oil by three methods:—

	Cyanacetic Acid Method. (Per cent.)	$NaHSO_3$ Method. (Per cent.)	Na_2SO_3 and $NaHCO_3$ Method. (Per cent.)
Non-aldehydic constituents, ...	18, free from citral.	24, citral present.	20, containing a little citral.
Citral, by difference, .	82	76	80
Citral, by direct determination, ...	75.4	65	77.5
Citral, loss in direct determination, ...	6.6	11	2.5

The cyanacetic acid method is to be preferred for the determination of the non-aldehydic constituents, and the alkaline sulphite method for the determination of the actual citral.

F. Tiemann states that the last method has the advantage

that citronellal does not affect the determination of the citral, but he denies the statement of Flatau and Labbé that a notable proportion (6 to 8 per cent.) of citronellal is present in lemon-grass oil.[1] Tiemann (*Ber.*, 1899, xxxii, 812) also points out certain differences in the behaviour of citral and citronellal with sulphites which may be utilised for their separation. Thus citronellal is not attacked by a 10 per cent. solution of sodium *sulphite* (Na_2SO_3, 7 aqua) *in presence of sodium bicarbonate*, and hence may be extracted together with the non-aldehydic substances by ether, whereas citral is completely converted under the same conditions into the unstable dihydrosulphonate already described. On the other hand, if a mixture of the aldehydes be shaken with excess of *concentrated* sodium sulphite and bicarbonate solutions, citronellal is converted into the normal bisulphite compound, which separates, and citral into the unstable dihydrosulphonate. If in this process the theoretical quantity or only a slight excess of sulphite be used, the citral compound is formed by preference, and the citronellal can be extracted unchanged by ether. By applying the process to lemon-grass oil, and shaking the residue freed from citral with a concentrated solution of sodium sulphite and bicarbonate, Tiemann obtained 0.2 gramme of the citronellal bisulphite-compound from 300 grammes of oil. If a mixture of the aldehydes be shaken with sodium sulphite solution while a current of carbon dioxide is passed through it, the citral is converted into the unstable dihydrosulphonate, while the citronellal forms the hydrosulphonate, which is not decomposed by caustic soda. If methyl-heptenone be also present (as in lemon-grass oil), the citral may be extracted by a 10 per cent. solution of sodium sulphite containing bicarbonate, the citronellal by a concentrated solution of the same kind, and finally the methyl-heptenone by an ice-cold solution of sodium bisulphite in 1½ parts of water.

Burgess and Child have adopted the following modifications of the bisulphite method and of the sulphite method of F. Tiemann for the determination of the aldehydes (citral, &c.) in lemon oil. Both methods are stated to yield almost theoretical results when the following details are adhered to carefully:—

(1.) In the determination of the aldehydes by the sodium bisulphite method, a 40 per cent. solution of the reagent is most convenient, and a strongly acid solution should be avoided.

[1] According to Flatau and Labbé (*Bull. Soc. Chim.*, 1898, p. 1012; 1899, xxi, p. 77), if the normal bisulphite compounds of citral and citronellal are treated with a solution of barium chloride, citryl sulphite remains in solution while the citronellal is precipitated quantitatively as $Ba(SO_3, C_{10}H_{19}O)_2$, but Tiemann (*Ber.*, 1899, xxii, 812) states that the normal bisulphite compound of citral gives a copious precipitate with barium chloride, though the precipitation is not complete; while the precipitation of the normal citronellal compound is not perfect.

Twenty-five cc. of lemon oil is mixed with 75 cc. of 40 per cent. sodium metabisulphite solution and 25 cc. of sodium sulphite (made by exactly neutralising sodium bisulphite solution with a 10 per cent. solution of sodium hydroxide) in a suitable flask. (See *Analyst*, 1900, page 197.) The temperature is then raised to about 70° C., and the solution thoroughly shaken for one hour. The addition of sodium sulphite is indispensable, owing to the fact that it forms a soluble sulphonic-acid compound and a clear meniscus is thus obtained. The oil is then raised into the measuring burette, and the diminution in volume gives the amount of total aldehydes.[1] A correction must be made for the solubility of the terpenes in solution. Burgess and Child subtract 0.35 cc. from the reading, but it is advisable for each worker to determine this correction.

(2.) The following method depends upon the fact, discovered by F. Tiemann, that if citral be agitated with a neutral solution of sodium sulphite, a soluble sodium sulphonic acid salt is produced. Burgess and Child have taken advantage of the formation of sodium hydroxide in the reaction to make an addition

$$C_9H_{15}.CHO + 2Na_2SO_3 + 2H_2O = C_9H_{17}.(NaSO_3)_2.COH + 2NaOH.$$

of phenolphthaleïn to the solution, to indicate the point when all the citral has combined to form the soluble compound. For the determination a saturated solution of sodium sulphite is prepared, and, if acid, is neutralised with a solution of sodium hydrate until a faint pink colour is permanently maintained with phenolphthaleïn. To 50 cc. of this solution 25 cc. of the oil is added, and two drops of an alcoholic solution of phenolphthaleïn. The whole is then heated on the water-bath nearly to boiling-point, with constant shaking. A deep-red colour almost at once appears, showing that the action has commenced. A few drops of sulphurous acid are then cautiously added, and the heating continued until no further colour is produced after a further addition of the sulphurous acid. The oil is then measured as described above. The obvious advantage of this method is that the end of the reaction may be ascertained to a certainty, while the bisulphite process depends on the continual shaking for a period of not less than one hour.[2]

[1] This method may also be used for solutions containing high percentages of citral, using from 5 to 20 cc. of the solution and measuring in a Hirschsohn or similar flask.

[2] H. E. Burgess has published further modified details of his sulphite process for the determination of aldehydes and ketones in essential oils (*Analyst*, 1904, p. 78). The method is carried out in a 200 cc. flask, having a graduated neck (5 cc. in $\frac{1}{10}$ cc.), and a side-tubulure, reaching to the bottom of the flask, for the introduction of the oil, reagents and water. 5 cc. of oil is employed and the process carried out as described in the text, dilute acetic acid being used to neutralise the alkalinity of

Other processes for the determination of citral in essential oils have been suggested, namely, the formation of the oxime with hydroxylamine in alcoholic solution and subsequent titration of the excess of hydroxylamine with hydrochloric acid; and the cyanacetic acid process of Tiemann already described (page 339). The process is described in detail in the *J. S. C. I.*, 1901, page 1176. S. Sadtler's method is described under "Lemon Oil," page 432. See also G. Romeo (*Chem. and Druggist*, 1905, p. 408).

Burgess and Child obtained the following results by the foregoing methods (*J. S. C. I.*, 1901, xx, page 1179):—

Nominal Percentage of Citral in Lemon Terpenes.	Sodium Bi- and Mono-sulphite. I.	Sodium Sulphite. II.	Hydroxylamine. III.	Cyanacetic Acid. IV.
2.5	2.2 (2.1)[1]	2.2 (2.1)[1]	2.6 (2.4)[1]	
5.0	4.4 (4.2)	4.0 (4.2)	5.0 (4.8)	
7.5	6.5 (6.3)	6.4 (6.3)	7.1 (7.2)	
10.0	8.6 (8.6)	8.4 (8.6)	9.6 (9.6)	
Commercial Citral,	84 %	84 %		100 %
Terpeneless Lemon Oil,	46.5 %	45.5 %	46.6 %	62 %[2]
Lemon-grass Oil,	75 %	75 %		97 %

CYCLIC TERPENE ALCOHOLS.

The bodies of this class occurring naturally in essential oils are tabulated on page 250.

BORNEOL. CAMPHOL. Bornyl Alcohol. $C_{10}H_{17}.OH$

This compound is a secondary alcohol and has probably the constitution shown on page 345.

Borneol occurs in the pith-cavities of *Dryobalanops camphora* and allied species growing in the Malay Archipelago. It also occurs in the oils of valerian and rosemary (4 to 5 per cent.)

the solution as it develops. The oil is finally brought up into the neck of the flask and its volume read off when cold. Oils such as lemon, citron, lime and orange cannot well be assayed direct, so that a process of fractionation under reduced pressure (apparatus in figs. 1, 2, p. 227) is first carried out, the flask and its contents being heated gently by means of an oil-bath. The last 20 per cent. of oil is distilled under normal pressure *in a current of steam, and the absorption process then followed* on 5 cc. of the separated oil-fraction, the calculation being finally referred to the original sample. The method gives good results.

[1] The figures in brackets show the calculated citral present.

[2] See E. J. Parry (*J. S. C. I.*, 1901, p. 1182).

and in the essential oil of Virginian snake-root (*Aristolochia serpentaria*).

Borneol forms the main constituent of "*Borneo camphor*." This, as imported, contains from 2 to 3½ per cent. of resin and other impurities, from which the borneol can be separated by sublimation.[1] Borneol may also be obtained by the action of sodium or of alcoholic potash[2] on common camphor.

Borneol forms regular crystals which are lighter than water. It has an odour like that of camphor and a pungent peppery taste. Borneol melts at 206° to 207° and boils at 212° C.; but it sublimes readily below its melting-point and condenses in hexagonal plates.

Borneol is very sparingly soluble in water, but soluble in alcohol, ether, and petroleum-spirit.

Borneol is optically active. The alcoholic solution of the natural substance has a specific rotation of $[a]_D = + 33°$, while that of the artificial product is + 43°. But natural *lævo-rotatory* borneol occurs nearly pure in *Ngai camphor*, and less pure in *Bang Phien*. It is also present in the oils of lavender, rosemary, spike, &c. The fusel oil of the spirit obtained by the fermentation of the sugar of madder contains *l*-borneol, which is said by Haller also to occur in the forms of acetate, formate, and valerate in the oil of valerian.

According to Haller, a racemoid modification of borneol, consisting of a mixture of dextro- and lævo-borneols in equal proportions, is obtained by the distillation of the crude colophene resulting from the action of sulphuric acid on turpentine oil.

An optically-inactive borneol, melting at 199°, was obtained from colophony by Armstrong and Fielden.

R. Stockman (*Jour. Physiol.*, ix, 65) found that dextro-, lævo-, and racemic-camphol prepared from turpentine oil produced identical physiological effects.

Isoborneol.—The borneol obtained by the reduction of camphor is stated to contain an admixture of a modification known as *iso-borneol*, which is also obtained by warming camphene with acetic acid and a little sulphuric acid, and decomposing the bornyl acetate formed by alcoholic potash. This reaction is employed by Bertram and Walbaum (*Jour. prakt. Chem.* [2], xlix, 15) for the detection of camphene in the oils of lemon, ginger, etc.

Isoborneol agrees with the ordinary modification in yielding camphor, &c., on oxidation by dilute nitric acid, but according

[1] A terpene or mixture of terpenes, sometimes called "borneene," occurs in association with borneol, and is found concentrated in *Borneo camphor oil*, which differs from the similar product associated with laurel-camphor by not yielding crystals on exposure to air.

[2] It is stated that the portions of artificial borneol obtained at the beginning and end of the process are dextro-rotatory, while the intermediate fractions are lævo-rotatory.

to Bertram and Walbaum (*loc. cit.*, abst. *Jour. Chem. Soc.*, lxvi, i, 204) exhibits the following differences:—

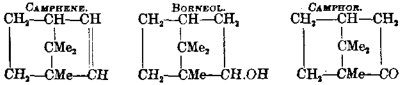
	BORNEOL.	ISOBORNEOL.
Crystalline form,	Hexagonal.	Hexagonal laminæ.
Melting-point; ° C.,	203	212
Boiling-point; ° C.,	212	—
Solubility in benzene, at 0° C.,	1 : 7	1 : 3
Solubility in petroleum-ether at 0° C.,	1 : 10	1 : 4
Melting-point of chloral compound; ° C.,	55 to 56	liquid
Melting-point of bromal compound; ° C.,	98 to 99	71 to 72
Acetate; melting-point; ° C.,	29	liquid
Acetate; boiling-point at 15 mm. pressure; ° C.,	106 to 107	107

Dehydrating agents convert isoborneol into *camphene*, whereas *borneol is unaffected. Isoborneol is converted into the corresponding* ether when boiled with sulphuric acid and methyl or ethyl alcohol, whereas borneol does not yield ethers by this treatment.[1]

L. A. Tschougaef (*Bull. Soc. Chem.*, xxvi, 298; abst. *J. S. C. I.*, *1901, p. 832) purifies borneol from isoborneol* by converting the alcoholate of borneol into methyl bornyl-xanthate, when steam-distillation removes the isoborneol. When heated with alcoholic potash and the liquid acidified the methyl ester yields borneol.

Borneol yields two additive-products with bromine, as also a *hydrobromide* containing $C_{10}H_{18}O,HBr$, which is decomposed into its constituents by the slightest trace of water. By the action of phosphorus pentachloride borneol is converted into a mixture of isoborneol and *bornyl chlorides*, $C_{10}H_{17}Cl$, and this on being heated to boiling with aniline yields the solid hydrocarbon *camphene*, $C_{10}H_{16}$. Hence borneol and camphor are respectively the *secondary alcohol* and the *ketone* of the parent hydrocarbon camphene. The following are the formulæ of the three bodies, according to Bredt. Other formulæ for camphene are given on page 259.

CAMPHENE. BORNEOL. CAMPHOR.



[1] According to F. W. Semmler (*Ber.*, 1900, xxxiii, 774), isoborneol on being heated with zinc-dust at 220° yields, as the chief product, *isodihydrocamphene*, $C_{10}H_{18}$, melting at 85°; whereas borneol remains unchanged when similarly treated. Since zinc is capable of removing oxygen from tertiary alcohols only (abst. *J. C. S.*, 1894, i, 611), the view that borneol and isoborneol are physical isomerides is untenable, the former being a secondary and the latter a tertiary alcohol.

Bornyl Esters.—When treated with the concentrated fatty acids, or preferably the corresponding anhydrides, borneol readily yields a series of esters having a pleasant camphoraceous odour. Some of these esters occur naturally in essential oils, and in some cases are present in considerable proportion. Thus:—

Ester.	Formula.	Boiling-point; ° C.		Sp. Gravity at 15° C.	Occurrence.
		At 760 mm.	At 10 mm.		
Bornyl Formate, . . .	$C_{10}H_{17}.CHO_2$	225 to 230	90	1.013 (1.017)	Valerian oil.
Bornyl Acetate, ...	$C_{10}H_{17}.C_2H_3O_2$	235 to 240	98	0.991	Pine-needle and Valerian oils.
Bornyl Propionate, . .	$C_{10}H_{17}.C_3H_5O_2$	. .	109 to 110	0.979	Valerian oil.
Bornyl Butyrate, . . .	$C_{10}H_{17}.C_4H_7O_2$	. .	120 to 121	0.966	
Bornyl Valerate, . . .	$C_{10}H_{17}.C_5H_9O_2$	255 to 260	128 to 130	0.956	Valerian Oil.

Bornyl Formate is liquid at ordinary temperatures. *Bornyl acetate* forms rhombic prisms which melt at 29° to a viscous liquid having the peculiar aroma of pine-needle oil. Bornyl acetate is obtained by heating borneol to 150° with acetic anhydride. It also results from the action of silver acetate on bornyl chloride, and of acetyl chloride on borneol.

Bornyl Ether or *Bornyl Oxide*, $(C_{10}H_{17})_2O$, is stated by Bruylants to occur in valerian oil. It is a viscous liquid, boiling at 285° to 290°, and is unaffected by heating with caustic potash.

TERPINEOL. Cinyl Alcohol. $C_{10}H_{17}.OH$

Terpineol is an unsaturated tertiary alcohol isomeric with borneol (page 343). A dextro-rotatory variety, either free or as an acetic ester, occurs naturally in the oils of lovage, marjoram, Malabar cardamoms, cajuput, and valerian.[1]

Terpineol is a colourless, strongly-refractive, optically-inactive liquid of 0.940 specific gravity at 15° C., having a very fragrant odour of hyacinth or lilac-flowers, especially when diluted. By cooling to —50° C. terpineol yields crystals melting at 34° to

[1] Terpineol may be obtained artificially in an impure state by heating terpin hydrate with hydrochloric acid, very dilute sulphuric acid, potassium sulphate, &c. It may also be prepared by boiling 25 grammes of terpin hydrate with 50 cc. of aqueous phosphoric acid, avoiding prolongation of the treatment, which would result in the formation of cineol (isomeric with terpineol) and terpinolene.

Terpineol may also be obtained by boiling cinene dihydrochloride (page 272) with water or alcoholic potash.

35° C.[1] Contact with these causes the solidification of terpineol at the ordinary temperature.[2] Terpineol is not attacked by alkalies or fatty acids, and owing to this fact and its high boiling-point (218°–219° C.) it is extensively employed for scenting toilet soaps.

Terpineol is practically insoluble in water, but dissolves readily in alcohol, ether, hydrocarbons and fatty oils.

By treatment with hydrochloric acid gas, terpineol is converted into cinene dihydrochloride (page 272), and by similar treatment with hydriodic acid into the compound $C_{10}H_{18}I_2$, melting at 77° C.

In presence of dilute hydrochloric acid, terpineol unites with the elements of water to form *terpin*, $C_{10}H_{18}(OH)_2$. Terpineol also unites with two atoms of bromine to form an unstable compound which is converted by excess of the reagent into *cinene tetrabromide*, $C_{10}H_{18}Br_4$.

TERPIN. Dipentenyl Glycol. $C_{10}H_{18}(OH)_2$

When oil of turpentine is exposed to the action of the air or other oxidising agents for some time, terpin is formed. Thus if eight parts of turpentine oil be mixed with two parts of alcohol[3] and two of nitric acid of 1.3 specific gravity, and exposed to low temperature for some days in shallow dishes, crystals of *terpin hydrate* separate.[4] Either dextro- or lævo-pinene (or the corresponding turpentine oil) may be employed for the preparation of terpin hydrate, but it cannot be obtained from limonene.

Terpin Hydrate, $C_{10}H_{20}O_2 + H_2O$, forms large, transparent, monoclinic prisms, sparingly soluble in cold and readily in boiling water, and very soluble in alcohol. It dissolves in 100 parts of ether and in 200 of chloroform. When heated to 116°–117°, terpin hydrate melts with loss of water, and on cooling solidifies to a vitreous mass of *anhydrous terpin*.

On distilling terpin hydrate, the water of crystallisation first passes over, and at 256° anhydrous terpin distils, solidifying on cooling to a hard mass, which melts at 102° (104° to 105°), is very hygroscopic, and readily combines with water.

[1] Isomers melting respectively at 70° and 32° C. have been described by Wallach (See *Annalen*, 1902, p. 79.)

[2] It was formerly supposed that there was a marked difference between the solid and liquid varieties of terpineol, but a thorough study of the question (*Ber.*, 1895, p. 1781) has revealed the fact that the two forms are either geometrical isomers, or else that the liquid form contains traces of an impurity, which prevents it from solidifying.

[3] L. Kentmann substitutes one part of hydrogen peroxide solution for the alcohol prescribed in the text.

[4] G. and E. Rousset (abst. *J. Soc. Chem. Ind.*, 1899, p. 65) state that the alcohol may be dispensed with and the yield of terpin much increased by using a mixture of four parts of oil of turpentine, two of nitric acid, and two of water.

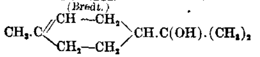
Terpin and terpin hydrate are optically inactive.

Terpin hydrate is official in the German, French, and other foreign Pharmacopœias. The United States Pharmacopœia (8th Rev.) states that if a few drops of sulphuric acid be added to its hot aqueous solution, the liquid will become turbid and develop a strongly aromatic odour. Terpin hydrate should not have an odour of turpentine,[1] and its hot aqueous solution should not redden blue litmus-paper (absence of adhering acid).

Terpin has the constitution of a glycol, and bears the same relation to terpineol that *propylene-glycol*, $C_3H_6(OH)_2$, bears to *allyl alcohol*, $C_3H_5(OH)$. By strong hydrochloric acid, terpin is converted into a cinene dihydrochloride. When boiled with water containing a trace of mineral acid, it is split up into water and *terpineol*, $C_{10}H_{18}O$. This change probably occurs as an intermediate reaction in all the varied metamorphoses which terpin suffers by treatment with acids, resulting in the formation of dipentene, terpinolene, terpinene, and cineol. When terpin, terpin hydrate, or terpineol is boiled for several hours with phosphoric acid of 1.12 specific gravity, a molecular change occurs with formation of the isomeric body *cineol*, $C_{10}H_{18}O$, which distils over as a lighter fraction. By careful regulation of the conditions of operating, it is possible in this manner to prepare the valuable product eucalyptol or cineol from pinene or turpentine oil.

The constitutional relationship between terpineol, terpin, and cineol is shown by the following formulæ:—

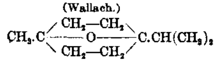
TERPINEOL.
(Bredt.)



TERPIN.

$$CH_3.C(OH)<\genfrac{}{}{0pt}{}{CH_2-CH_2}{CH_2-CH_2}>CH.C(OH).(CH_3)_2$$

CINEOL.
(Wallach.)



CINEOL. EUCALYPTOL. $C_{10}H_{18}O$

Cineol is identical with *cajuputol* (the chief constituent of oil of cajuput), and forms the greater part of oil of wormseed, from the unexpanded flower-heads (flower-buds) of *Artemisia maritima*

[1] A completely odourless product is best obtained by exposing the dry and powdered substance to the air until it loses its odour, when it is recrystallised from hot alcohol.

(see Vol. III, Part iii).[1] Cineol or eucalyptol is also present in large proportion in many eucalyptus oils,[2] and occurs, together with camphor and borneol, in the oils of rosemary and spike-lavender.

Cineol is a product of the action of boiling phosphoric and other mineral acids on terpin hydrate, which is itself readily prepared from turpentine oil.

Cineol is a colourless liquid, having a characteristic camphoraceous odour, and a pungent cooling taste. The specific gravity of liquid cineol at 15° C. is 0.930. When exposed to a low temperature, it solidifies to a mass of colourless needles, which melt at —1° C. Cineol boils at 176° to 177°. Its refractive index is 1.4559, and it is optically inactive.

Cineol is soluble in all proportions in alcohol, glacial acetic acid, ether, chloroform, benzene, carbon disulphide and fatty and volatile oils. It is not dissolved by water nor by aqueous solutions of caustic alkalies. Cineol is itself a solvent of caoutchouc, guttapercha, benzoic and salicylic acids, phenol, &c.

Eucalyptol, from the oil of Eucalyptus globulus or allied species, is now somewhat extensively employed in medicine, the internal dose ranging from two to five grains. In addition to the characters given above, the alcoholic solution of the commercial article should be neutral to litmus and should not develop a brownish or violet colour on the addition of a drop of tincture of ferric chloride. Such a reaction would indicate the presence of phenols, the amount of which can be ascertained by shaking the sample with an equal measure of a normal solution of caustic soda, in which cineol is insoluble.

Cineol unites with bromine to form the compound $C_{10}H_{18}O,Br_2$ (distinction from terpin), which crystallises in red needles and prisms that readily decompose into water, bromine, and cinene, one-half of the last product uniting with bromine to form *cinene tetrabromide*, $C_{10}H_{16}Br_4$.

When cineol is agitated with a strong solution of iodine in potassium iodide, a pasty mass is formed in which green lustrous crystals may be observed. These may be dried partially on a

[1] Fairly pure cineol may be obtained by saturating rectified oil of wormseed with dry hydrochloric acid gas. The resultant crystalline mass is freed from the fluid portion by pressure, and treated with hot water. The regenerated cineol is washed by agitation and distilled in a current of steam, after any adhering hydrochloric acid has been neutralised by soda.

[2] Eucalyptol may be conveniently prepared from such of the oils of eucalyptus as contain it by treatment with a strong solution of phosphoric acid (preferably of 1.785 specific gravity), when a crystalline compound of the composition $C_{10}H_{18}O, H_3PO_4$ crystallises out. This is separated and decomposed by hot water, when the liberated eucalyptol separates as an oily layer, which, after washing by agitation with water, is practically pure. (L. R. Scammel, *Brit. Patent*, 1894, No. 14138.)

porous plate, but they rapidly deliquesce. The reaction may be employed for the detection of cineol.

By treatment with oxidising agents cineol is readily converted into *cineolic acid*, $C_{10}H_{16}O_5$.

Cineol combines with iodol to form a yellowish-green additive compound of the formula $C_{10}H_{18}O, C_4I_4NH$, which melts at 112°, and may be used for the detection of cineol in oils, &c.

Cineol does not react with phenyl-hydrazine or hydroxylamine, nor does it combine with bisulphites. It is not affected by sodium or by benzoyl chloride below 120°, but at higher temperatures it yields benzaldehyde, hydrochloric acid, and cinene. When heated with alcoholic sulphuric acid, cineol yields terpinene and terpinolene.

From the foregoing characters it appears that cineol is neither a phenol, a ketone, an aldehyde, nor a true alcohol. The oxygen-atom appears to be wholly indifferent. The constitution of cineol is probably that of cinyl oxide, $C_{10}H_{18}:O$, which bears the same relation to terpin that ethylene oxide bears to glycol.

MENTHOL. MENTHYL ALCOHOL. $C_{10}H_{19}.OH$

Menthol has the constitution of a methyl-isopropyl-phenol hexahydride:—

$$CH_3.CH\left\{\begin{array}{l}.CH_2.CH_2\\.CH_2.CH(OH)\end{array}\right\}CH.CH.(CH_3)_2$$

Menthol occurs, together with menthone[1] and the hydrocarbon menthene, in peppermint oil, and separates in crystals on cooling

[1] **MENTHONE**, $C_{10}H_{18}O$; or $CH_3.CH\left\{\begin{array}{l}CH_2.CO\\CH_2.CH_2\end{array}\right\}CH.C_3H_7$

This substance is a body of ketonoid constitution, which occurs in American oil of peppermint (10 to 12 per cent.). It may be prepared by the action of chromic acid mixture on peppermint oil. Menthone is an oily liquid smelling like diluted peppermint oil. Two modifications of it exist, of opposite optical activities, and apparently differing in certain other respects, as shown in the following table:—

	DEXTRO-MENTHONE.	LÆVO-MENTHONE.
Optical activity; $[\alpha]_D$,	+21° (26° to 28°)	—26°
Refractive Index,	1.4528	1.4496
Specific gravity,	0.897 at 20°	0.894
Boiling-point,	206°	208°
Oxime, $C_{10}H_{18}(NOH)$,	liquid; slightly lævo-rotatory.	M. pt. 59; lævo-rotatory.
Amine, $C_{10}H_{19}NH_2$,	liquid; B. pt., 206°	liquid; B. pt., 206°

Lævo-menthone occurs in oil of buchu.

By the action of phosphoric anhydride on the oximes the corresponding *nitriles*, $C_9H_{17}.CN$, are obtained. From the dextro-rotatory variety Wallach prepared the open-chain alcohol *mentho-citronellol*, $C_{10}H_{19}.OH$, isomeric and possibly identical with citronellol.

The *semicarbazone* from dextro-menthone melts at 184° and has the formula $C_{10}H_{18}:N.NH.CONH_2$.

the oil.[1] The menthol from American oil of peppermint (derived from *mentha piperita*), for which the name of *pipmenthol* has been suggested, usually forms snow-white acicular crystals, or stellate groups of white satiny needles, having the characteristic odour and flavor of peppermint.[2] The product from the Japanese and Chinese oils forms prismatic crystals closely resembling those of magnesium sulphate, and having a peculiar fragrant odour, suggesting a mixture of peppermint with some other members of the mint family.

Pure menthol volatilises slowly at the ordinary temperature, melts at 42° to 43°, and boils at 215.5° (Power). E. J. Parry gives the boiling-point of menthol as 212°, and the specific gravity as 0.890 at 15°.

Menthol is but slightly soluble in water, but imparts to the liquid its characteristic taste and smell. It dissolves readily in alcohol, ether,[3] carbon disulphide, and in fixed and volatile oils. The solutions are lævo-rotatory; $[\alpha]_D = -49.4°$ in 5 per cent. alcoholic solution at 22° C.

Menthol is not soluble in aqueous alkalies, a character which distinguishes it and permits of its ready separation from thymol and phenol.

The proportion of menthol contained in oil of peppermint, &c., is best ascertained by converting it into its acetic ester, as described on page 229.

Menthol is extensively employed as a remedy for neuralgic headache and other affections. It forms the active constituent of the "neuralgic crystals," which, however, are liable to considerable adulteration. Thus, in addition to a legitimate economisation of the menthol by forming the base of the pencil

[1] Oil of peppermint of European origin contains comparatively little menthol, but the Chinese and Japanese oils frequently form a semi-solid mass consisting of crystals of menthol saturated with liquid hydrocarbons. According to E. Charabot (*Compt. rend.*, cxxx, 518; abst. *J. S. C. I.*, 1900, page 372) the formation of esters appears to be a function of the green part of the peppermint plant while the oxidation of menthol to menthone is a function of the flowers.

[2] According to the British Pharmacopœia (1898), menthol occurs in "colourless acicular crystals, usually more or less moist from adhering oil, or in crystalline masses." As pointed out by Schimmel & Co. (*Report*, Oct., 1898), this description gives official recognition to an impure article. The melting-point of menthol is given as 42°, and ought not to exceed 43° C. Menthol is further stated to be "entirely volatilised by the heat of a water-bath, and to acquire an indigo-blue or ultramarine colour when boiled with sulphuric acid diluted with half its volume of water, the acid itself becoming brown." F. B. Power regards this reaction as of "exceedingly doubtful value."

[3] Waste or impure menthol may be purified by recrystallisation from its solution in methylated ether, benzene, petroleum-spirit, carbon disulphide, or acetone. When ether is employed as the solvent, the menthol crystals can be freed from all foreign odour by a few hours' exposure to the air. (A. W. Gerrard, *Pharm. Jour.*, 1900, lxv, 163.)

of paraffin-wax, the menthol itself is sometimes mixed with paraffin; and fatty matters, thymol, and other substances have also been added (*Pharm. Jour.* [3], xv. 365, 686). To ascertain the quality of a pencil, a portion of the substance should be scraped from the surface and its melting-point determined. The commercial article fuses at 41° to 43° C. An admixture of paraffin-wax notably raises the melting-point, unless some other adulterant is also present. On heating a weighed portion of the exterior of the pencil to 100° C. the menthol will volatilise, and its quantity may be ascertained from the loss in weight, none of the probable admixtures, such as fatty matters, spermaceti, paraffin-wax, salicin, salicylic acid, thymol, &c., being sensibly volatile at 100°. Mineral matters, such as magnesium sulphate, which is said to have been used as an adulterant of menthol, will remain on heating the sample to dull redness in the air.

The ready solubility of menthol in cold rectified spirit is a test of some value, as many adulterants (*e.g.*, paraffin, spermaceti, and fats) are insoluble in that menstruum. The alcohol should be heated to boiling to ensure the complete solution of the menthol, and the liquid then allowed to cool. By operating in this manner the test may be made quantitative.

Salicin may be readily recognised by its bitter taste, solubility in water, and the red colour it assumes when touched with strong sulphuric acid.[1] *Salicylic* and *benzoic acids* will communicate an acid reaction to the alcoholic solution of the sample. They may be isolated by treating the sample with aqueous soda, agitating the liquid with ether, separating the ethereal layer, and acidulating the concentrated aqueous liquid with hydrochloric acid, when they will be thrown down as a bulky white precipitate readily soluble in ether. *Thymol* may be separated from menthol by treating the sample with a hot solution of soda, which dissolves the thymol only. *Thymol may be detected by Eykman's test* (page 356).

Menthol pencils adulterated with the above-named substances occasion an intense prickling sensation on the skin, quite distinct from the cooling sensation produced by pure menthol. By reaction with acids, menthol readily yields *esters* and by treatment with phosphorus pentachloride or hydrochloric acid it is converted into *menthyl chloride*, $C_{10}H_{19}Cl$. By distillation with zinc chloride or phosphoric anhydride, menthol is converted into the hydrocarbon *menthene*, $C_{10}H_{18}$, a dextro-rotatory liquid which has an odour of cymene, boils at 167° C., and combines with bromine to form the addition-product $C_{10}H_{18}Br_4$. This is converted into *cymene*, $C_{10}H_{14}$, by heating and distilling the product with sodium.

[1] Salicin is stated by P. W. Bedford to give a more opaque appearance to menthol cones than is usual in pure menthol. Salicin may also be recognised by its infusibility. Paraffin may be detected by the touch.

SESQUITERPENE ALCOHOLS. $C_{15}H_{25}.OH$

A series of compounds of the above formula exist in certain essential oils. They are sometimes called *sesqui-camphors,* since the majority of them resemble ordinary camphor in their physical characters, but in chemical constitution they are undoubtedly alcohols.

The sesquiterpene alcohols are closely related to the sesquiterpenes, $C_{15}H_{24}$, and are converted into these hydrocarbons when heated with phosphoric anhydride or other dehydrating agents.

The following table shows the chief sources and the physical characters of the best-known members of the group, and the names of the sesquiterpenes into which they are converted by dehydrating agents:—

SESQUITERPENE ALCOHOL.	CHIEF SOURCES.	M. PT., ° C.	B. PT., ° C.	OTHER CHARACTERS.	SESQUITERPENE.
Cubebol (Cubeb Camphor), ...	Cubebs Oil.	65 to 67	248	Lævo-rotatory; crystallises in rhombs.	Cubebene (Cadinene ?).
Cedrol (Cedar Camphor),...	Cedar-wood Oil.	85 to 86 (Schimmel)	252	Silky needles; aromatic odour; dextro-rotatory.	Lævo-cedrene.
Cypress-Camphor, ...	Cypress Oil.	86 to 87	291	Long needles; inactive.	Dextro-cedrene.
Ledenol (Ledum Camphor), ...	Marsh-tea Oil.	104 to 105	282	Odourless prisms; sublimes in needles.	Ledene.
Patchoulol (Patchouli Camphor),...	Patchouli Oil	56	296	Lævo-rotatory; hexagonal prisms.	Patchoulene (cadinene ?).
Ylang-Ylang Camphor,....	Ylang-Ylang Oil.	138	...	...	...
Santalol,.......	Santal-wood Oil.	liquid.	168 to 170 at 11 mm.	Spec. gravity 0.979; optical rotation,—18°.	

All the above alcohols can be acetylated more or less readily. Santalol differs from the other members of the group in being liquid at ordinary temperatures. At least two isomers or closely-allied bodies differing in optical activity are present in so-called "santalol," the chemistry of which is described at greater length under "Santal-wood Oil."

PHENOLS AND PHENOLIC ETHERS.

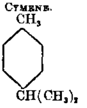
A considerable number of substituted phenols occur as constituents of essential oils. They may be classified in two groups, namely, those compounds in which two of the hydrogen-atoms of the benzene-chain are replaced respectively by *methyl* and

propyl or *isopropyl*, and those in which an atom of the benzenic hydrogen is replaced by *allyl* or its isomer *propenyl*. Substitution by ethyl does not seem to occur. In the case of the phenolic ethers of essential oils, the phenolic hydrogen appears to be invariably replaced by methyl.

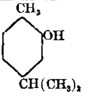
Methyl-propyl Phenols.

Several bodies existing naturally in essential oils have the constitution of *methyl-isopropyl-hydroxybenzenes* (cymophenols). This structure may be regarded as established in the cases of thymol and carvacrol.[1] Borneol, menthol, and cineol also undoubtedly contain methyl and propyl-groups, but their relation to benzene is not so completely established as would appear from certain formulæ which have been proposed for them. The isomerism of carvacrol and thymol is exhibited by the following formulæ, whence it appears that the former is the ortho- and the latter the meta-variety of the same phenol. The para-position in each case is occupied by isopropyl.

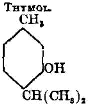
CYMENE.



CARVACROL.[1]



THYMOL.



THYMOL. THYMYL ALCOHOL. META-CYMOPHENOL. $C_{10}H_{13}OH$
(See page 251.)

Thymol is the stearoptene of thyme oil, and is also contained in the volatile oils of horse-mint, wild-thyme, ajowan, &c. It may be extracted from thyme oil by agitation with an equal measure of a 20 per cent. solution of caustic soda. The aqueous layer is separated and treated with excess of dilute acid, when the thymol rises to the surface as an oily layer. Another plan is to expose the crude oil to a temperature of 0° C., when the thymol crystallises out, and may be purified by re-crystallisation from alcohol or glacial acetic acid.

Thymol is prepared synthetically by treating dibromoparacymene with fuming sulphuric acid, and acting on the resulting dibromoparacymene-sulphonic acid with zinc-dust and ammonia to eliminate the bromine. The product is then fused with caustic potash, when the potassium thymolate obtained is decomposed by sulphuric acid, and the resulting thymol purified by crystallisation.

Thymol is homologous with phenol and cresol, which bodies it closely resembles in its general properties. It forms a series of

[1] Carvacrol is described in detail on page 384.

crystallisable salts, many of which distil unchanged. Thymol is a powerful antiseptic, its preservative power being ten times as great as carbolic acid according to Bucholz, and four times as great according to Willmott. It acts as a caustic on the lips and mucous membrane, but does not irritate the skin like carbolic acid.

Thymol forms large colourless crystalline plates having a feeble aromatic smell and burning peppery taste. It melts, when pure, at 51° C.,[1] and does not readily resolidify unless touched by a solid body or a crystal of thymol. It boils at about 232° C. Solid thymol is slightly heavier than water (sp. gr. 1.028), but in the fused state it is rather lighter. The density appears to be somewhat variable. In water, thymol is scarcely soluble, requiring about 1200 parts of cold or 900 of boiling water. Even this dilute solution is powerfully antiseptic. Rectified spirit dissolves its own weight of thymol, the greater part separating again on dilution. An alcoholic solution of thymol of about one per cent. strength is miscible with water in all proportions. Thymol is very sparingly soluble in glycerol, requiring 120 parts for solution. The liquid is precipitated by an equal measure of water, but is perfectly miscible with four measures. The solution so obtained is a useful lotion.

Thymol is readily soluble in glacial acetic acid. It is also freely dissolved by ether, chloroform, benzene, petroleum-spirit, and oils. When thymol and camphor are triturated together, a syrupy liquid is obtained, which is readily miscible with vaseline and similar preparations. Thymol is insoluble in small quantities of alkaline liquids, but dissolves in presence of an equivalent amount of caustic soda (40 of soda to 150 thymol), forming a soluble crystallisable compound, $C_{10}H_{13}.ONa$, which is decomposed by acids with separation of the thymol.

Thymol is not dissolved by solution of ammonia, but it absorbs ammonia gas with liquefaction, and re-solidifies when the ammonia is allowed to escape by exposure to air.

When thymol is heated to 100° with strong sulphuric acid, it is converted into *thymol-parasulphonic acid*. (A small quantity of thymol-disulphonic acid is simultaneously formed.) If the solution be diluted with ten times its measure of water, and the liquid digested with excess of white lead and filtered, the filtrate contains lead thymo-sulphonate and acquires a beautiful violet-blue colour on adding a drop of ferric chloride. Phenol gives a similar reaction.

With excess of bromine-water, solutions of thymol yield a yellowish-white precipitate of a di-bromo-derivative.[2]

[1] The British Pharmacopœia states that thymol, when placed in warm water, melts at a temperature of from 43.3° to 51.7° C.

[2] E. Zdarek (*Zeit. anal. Chem.*, xli, 227; abst. *Analyst*, 1902, p. 257) has applied this reaction to the determination of thymol (*Cf.* p. 473). The method is essentially that of Koppeschaar, as employed in the determination of phenol (Vol. II, Pt. ii), and of salicylic acid (this Volume, page 75).

A delicate test for thymol consists in heating the solution with half its measure of glacial acetic acid, and at least its own measure of concentrated sulphuric acid, when a fine violet-red coloration will be produced, not destroyed by boiling, and having a characteristic absorption-spectrum. J. F. Eykman modifies this test by dissolving a little of the sample in 1 cc. of glacial acetic acid, and adding five or six drops of strong sulphuric acid and one drop of nitric acid, when, if thymol be present, at first a greenish and then a fine blue coloration will make its appearance in the lower part of the test-tube, and will spread throughout the liquid on shaking. Phenol gives a violet-red colour, but menthol, camphor, borneol, and salicylic acid give no colour-reaction when similarly treated.

Tested with the reagents for phenol (see Vol. II, Part ii), an aqueous solution of thymol gives the following reactions:—

Thymol gives no coloration with ferric chloride.

With ammonia and hypochlorites, strong solutions of thymol give a greenish colour, changing very slowly to blue-green and red, but with more dilute solutions a mere turbidity is produced on heating, without any colour resulting.

With sodium hypochlorite and aniline, thymol behaves like phenol.

Thymol in tolerably strong solutions (1 in 5000) gives a red or violet coloration or precipitate with Millon's reagent, but the reaction is far less delicate than with phenol, and the colour is destroyed by boiling.

Thymol reduces gold and platinum from their solutions (the latter only on boiling) far more readily than does phenol.

It appears from the above that *phenol* in presence of thymol may be best detected by its reaction with ferric chloride, and in very dilute solutions by ammonia and hypochlorite. In the concentrated state, thymol is distinguished from phenol by its less ready solubility in water, glycerin, and alkaline liquids, and by forming a liquid bromo-derivative. It may be separated from phenol by fractional distillation, and from *menthol* by treatment with excess of strong solution of caustic soda.

Allyl Phenols. Propenyl Phenols.

A number of bodies which exist in natural essential oils have the constitution either of allyl- or propenyl-phenols, or of methyl-esters of these compounds. Several bodies which contain the *allyl-group*, CH_2:CH.CH_2—, are convertible by molecular rearrangement into the corresponding compounds containing the isomeric *propenyl-group*, CH_3.CH:CH—. The transformation can usually be effected by boiling with alcoholic potash. Thus:—

Methyl-chavicol, $CH_2:CH.CH_2(C_6H_4.OMe)$,
yields *Anethol*, $CH_3.CH:CH(C_6H_4.OMe)$.
Safrol, $CH_2:CH.CH_2(C_6H_3:O_2:CH_2)$,
yields *Iso-safrol*, $CH_3.CH:CH(C_6H_3:O_2:CH_2)$.
Eugenol, $CH_2:CH.CH_2(C_6H_3(OH).OMe)$,
yields *Iso-eugenol*, $CH_3.CH:CH(C_6H_3(OH)OMe)$.
Apiol, $CH_2:CH.CH_2(C_6H(OMe)_2:O_2:CH_2)$,
yields *Iso-apiol*, $CH_3.CH:CH(C_6H(OMe)_2:O_2:CH_2)$.

SUBSTANCE.	CHIEF SOURCES.	EMPIRICAL FORMULA.	CONSTITUTIONAL FORMULA.
Chavicol (Para-allyl-phenol),	Betel oil. Bay oil.	$C_9H_{10}O$.	$C_6H_2\left\{\begin{matrix}CH_2.CH:CH_2\\H\\H\\OH\end{matrix}\right.$
Methyl-chavicol,[1]	Sweet basil oil. Bay oil. Chervil oil.	$C_{10}H_{12}O$.	$C_6H_2\left\{\begin{matrix}CH_2.CH:CH_2\\H\\H\\OCH_3\end{matrix}\right.$
Anethol,	Anise, star-anise and fennel oils, &c.	$C_{10}H_{12}O$.	$C_6H_2\left\{\begin{matrix}CH:CH.CH_3\\H\\H\\OCH_3\end{matrix}\right.$
Chavibetol.[2] (Betel-pheool),	Betel oil.	$C_{10}H_{12}O_2$.	$C_6H_2\left\{\begin{matrix}CH_2.CH:CH_2\\H\\OH\\OCH_3\end{matrix}\right.$
Safrol,	Sassafras, Japanese camphor and star-anise oils, &c.	$C_{10}H_{10}O_2$.	$C_6H_2\left\{\begin{matrix}CH_2.CH:CH_2\\H\\O\\O>CH_2\end{matrix}\right.$
Eugenol,[2]	Clove and cinnamon-leaf oils, &c.	$C_{10}H_{12}O_2$.	$C_6H_2\left\{\begin{matrix}CH_2.CH:CH_2\\H\\OCH_3\\OH\end{matrix}\right.$
Methyl-Eugenol,	Hazel-wort oil (*Asarum Europæum*), bay oil, &c.	$C_{11}H_{14}O_2$.	$C_6H_2\left\{\begin{matrix}CH_2.CH:CH_2\\H\\OCH_3\\OCH_3\end{matrix}\right.$
Asarol (*Asarone*),	Hazel-wort oil, matico oil.	$C_{12}H_{16}O_3$.	$C_6H_2\left\{\begin{matrix}CH:CH.CH_3\\OCH_3\\OCH_3\\OCH_3\end{matrix}\right.$
Apiol (Parsley-camphor),	Parsley oil.	$C_{12}H_{14}O_4$.	$C_6H\left\{\begin{matrix}CH_2.CH:CH_2\\OCH_3\\OCH_3\\O\\O>CH_2\end{matrix}\right.$
Diosphenol,	Buchu oil.	$C_{10}H_{16}O_2$.	$C_9H_{14}\left\{\begin{matrix}OH\\COH\end{matrix}\right.$

[1] ESTRAGOL is an isomer of methyl-chavicol occurring in estragon or tarragon oil (*Ber.*, xxvii, R. 46; xxix, 344). It boils at 215° and yields anethol on heating with alcoholic potash.

[2] According to Gildemeister and Hoffmann, the formulæ for the isomers chavibetol and eugenol should be the reverse of those above given. That is, chavibetol should have the methoxyl-group in the meta- or third position and the hydroxyl-group in the para- or fourth, these positions being reversed in the formula of eugenol.

The preceding table shows the relationships of the more prominent members of this class which have been met with in nature. Their physical characters have been described in the table on page 251.

CHAVICOL. Para-Allylphenol. $C_3H_5.C_6H_4.OH$ (See page 251).

Chavicol forms from 30 to 40 per cent. of betel oil from fresh betel leaves,[1] and is the constituent to which betel oil owes its pleasant, characteristic odour. It is also stated to be present, together with methyl-chavicol or estragol, in bay oil (*Myrcia acris*). Chavicol is a colourless oil, moderately soluble in water, and but slightly soluble in ammonia. It has a refractive-index of 1.5441 at 20° C.

ANETHOL. Para-Propenylphenol Methyl-ester. $C_3H_5.C_6H_4.OCH_3$

Anethol occurs in admixture with more or less terpenes and other bodies, in the essential oils of aniseed (*Pimpinella anisum*), star-anise (*Illicium verum*), fennel, tarragon, &c. It is deposited in crystalline plates when these oils are cooled. Anethol has an odour resembling that of oil of anise. It undergoes oxidation on keeping. Freshly-prepared pure anethol congeals at about 21° C., and re-melts between 22.5° and 22.7°. It is optically inactive. Its refractive-index is 1.5615 at 18°. Anethol is only sparingly soluble in water, but dissolves easily in alcohol and ether. Anethol is readily polymerised by the action of sulphuric acid, stannic chloride, &c. By boiling with hydriodic acid, anethol yields methyl iodide and *anol*, $C_3H_5.C_6H_4.OH$, and by boiling with chromic acid mixture is converted into acetic acid and *anisic acid*, $C_6H_4(O.CH_3).COOH$. Anethol combines with bromine with production of a brom-anethol dibromide, $C_6H_3Br.(O.CH_3).(C_3H_5Br_2)$, which melts at 107°.

By boiling with alcoholic potash, anethol undergoes a molecular rearrangement, with conversion into the isomeric body *methyl-chavicol* (see page 357), which co-exists with anethol to a small extent in aniseed oil.

[1] CHAVIBETOL. Methoxy-chavicol. $C_3H_5.C_6H_3(OCH_3).OH$ (page 251). It is stated that while the phenol from fresh betel leaves is chavicol, the corresponding constituent of the oil from dried betel leaves is a methoxy-chavicol, which is present in the large proportion of 70 to 75 per cent., and is insoluble in water.

Chavibetol is isomeric with eugenol, these two compounds, together with safrol, being derivatives of *allyl-dioxybenzene*, $C_6H_3.(C_3H_5).(OH)_2$. Both chavibetol and chavicol, *in alcoholic solution*, react with ferric chloride with production of a fine coloration. In the case of the former, the coloration is deep bluish-green, and deep blue in case of chavicol. The coloration with chavicol in alcoholic solutions is obtained with some difficulty. In aqueous solutions, chavicol gives an intense blue coloration with ferric chloride, but no coloration is produced with chavibetol.

SAFROL. $C_{10}H_{10}O_2$ (See page 251.)

Safrol is the essential constituent of oil of sassafras, and is also present in camphor oil, the oil from star-anise, &c.

Safrol is a colourless liquid, but when cooled sufficiently it crystallises in large monoclinic prisms which melt at $+8°$ to $+12°$ C. *Safrol is neutral to litmus, optically inactive,* and has a fragrant odour of sassafras. Its refractive-index is 1.5384 at 17° C.

Safrol is official in the U. S. Pharmacopœia (8th Rev.), which describes it as having a specific gravity of 1.105 to 1.106 at 25° C. and boiling at about 233° C. On cooling to $-20°$ C., it should not melt below $+11°$ C. Safrol is further stated (U. S. P.) to be soluble in about 30 parts of 70 per cent. alcohol.

When gently heated with alcoholic potash, safrol is converted into *isosafrol,* the allyl group being isomerised to a propenyl group. Isosafrol is a liquid boiling at 246° to 248°, and solidifying at very low temperatures. Both safrol and isosafrol yield an intense red coloration when treated with strong sulphuric acid. Safrol is not altered by treatment with sodium, whereas isosafrol is readily reduced to *dihydrosafrol,* $C_{10}H_{12}O_2$.

Safrol is now manufactured on a considerable scale and in a condition of great purity. It is largely used in perfumery, for scenting toilet-soaps, and for the manufacture of heliotropin on a large scale.

Safrol is closely related to *piperonal* (heliotropin), *vanillin,* and *apiol.*[1]

EUGENOL. $C_3H_5.C_6H_3(OCH_3).OH$ (See page 251.)

This body, sometimes called *caryophyllic acid,* is the chief constituent of oil of cloves, of which it forms from 75 to 90 per cent. Eugenol also occurs in the oils of allspice, *Pimenta officinalis,* cinnamon-leaves (90 per cent.), and canella and massoya barks. It is likewise present in the leaves of *Illicium religiosum,* and in small proportion in the oils of camphor, sassafras, and cinnamon-bark.

For the preparation of eugenol, oil of cloves should be shaken with an alcoholic solution of caustic potash, and the resulting mass pressed between folds of blotting-paper, washed with alcohol, and decomposed by dilute hydrochloric acid. Eugenol may also be prepared by agitating three measures of oil of cloves with

[1] VANILLIN. PIPERONAL. SAFROL. APIOL.

$$C_6H\left\{\begin{array}{l}COH\\H\\OCH_3\\OH\\H\end{array}\right. \qquad C_6H\left\{\begin{array}{l}COH\\H\\O\\O\end{array}\!>CH_2\\ \;H\right. \qquad C_6H\left\{\begin{array}{l}C_3H_7\\H\\O\\O\end{array}\!>CH_2\\ \;H\right. \qquad C_6H\left\{\begin{array}{l}C_3H_7\\OCH_3\\OCH_3\\O\\O\end{array}\!>CH_2\right.$$

ten measures of a 10 per cent. solution of caustic potash. The oily layer, consisting of hydrocarbons, &c., is separated, and the eugenol liberated from the aqueous liquid by acidulating it with hydrochloric acid or passing a stream of carbon dioxide through it. The eugenol is then washed by agitation with water, and purified by distillation.

Eugenol may be obtained synthetically by the action of sodium-amalgam and water on coniferyl alcohol.

When freshly-prepared, eugenol is a colourless, oily, highly refractive liquid, having the characteristic smell and taste of cloves. It turns brown on exposure to air, and boils with slight decomposition at 247°, according to Idris and Parry, or 254° according to Schimmel. Its refractive-index is 1.5439 at 20°.

Eugenol is official in the U. S. Pharmacopœia (8th Rev.), which requires it to have a specific gravity of 1.072 to 1.075 at 25° C., and to be soluble in two parts of 70 per cent. alcohol. A clear solution, becoming turbid on exposure to air, should be obtained when one part of eugenol is dissolved in 12 parts of 5 per cent. sodium hydroxide solution, and 18 parts of water added. The filtered hot aqueous extract, when cold, should give no blue or violet colour with ferric chloride (absence of phenol).

Eugenol is very slightly soluble in water, but dissolves readily in alcohol, ether, and glacial acetic acid. It is also readily soluble in a dilute solution of caustic alkali (1 to 2 per cent. of KHO). *This character may be employed for the determination* of eugenol in oil of cloves, &c., and used as a test of its purity.[1] When shaken with ammonia, eugenol is converted into a yellow crystalline mass of a compound of the two.

On adding one drop of strong sulphuric acid to ten of eugenol a blue coloration is stated to be developed, changing, on addition of more acid, to a purple-red. Bromine-vapour colours eugenol blue.[2]

An alcoholic solution of eugenol gives a blue colour on addition of ferric chloride. It reduces ammonio-nitrate of silver, but not Fehling's solution.

Eugenol is stated to be a more powerful antiseptic than phenol. It can be taken internally in small doses without ill-

[1] In practice, a stronger solution of caustic soda (5 per cent.) is employed. *This dissolves certain neutral bodies in addition to eugenol,* but these may be removed by agitation with ether.

[2] When eugenol is treated with bromine, it yields *dibrom-eugenol dibromide*, $C_6HBr_2(OH)(OCH_3)(C_3H_5Br_2)$. The two bromine-atoms in the allyl-group can be removed from this compound by treatment with zinc-dust, *dibrom-eugenol* being formed. On the other hand, on treating isoeugenol, in the cold, with bromine, monobromo-isoeugenol dibromide is formed, and this compound does *not* give up bromine on treatment with zinc-dust.

effects, but in larger quantities it occasions headache and vertigo. It passes into the urine as *eugenol-sulphuric acid*, which rapidly splits up into its constituents.

When boiled with alcoholic potash, engenol is converted (incompletely) into *iso-eugenol*, a body in which the *allyl-group* has undergone molecular rearrangement and conversion into the *propenyl-group* (see page 356). Iso-eugenol boils at 260° and is coloured olive-green by ferric chloride.

By the action of potassium permanganate, eugenol is oxidised with formation of vanillin, homo-vanillin, and vanillic acid. Eugenol forms the starting-point of several commercial methods of preparing artificial vanillin.

Methyl-eugenol (see pp. 251, 357) is a constituent of several essential oils.

Determination of Eugenol.

The determination of eugenol is of practical importance for the valuation of oil of cloves and other essential oils, but is complicated by the presence of eugenyl esters (acetate, &c.) as well as free eugenol. Hence processes which determine the free eugenol only give lower results than those which effect, in addition, a partial or complete determination of the combined eugenol.

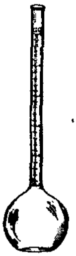


FIG. 4.

J. C. Umney has proposed the following simple method for the determination of the eugenol in oil of cloves (*Pharm. Jour.* [3], xxv, p. 950):—A known quantity (10 cc. at 15° C., or 10 grammes) of the sample is mixed, in a 100 cc. flask with a long narrow neck graduated in tenths of a cc. (Fig. 4), with a 10 per cent. aqueous solution of caustic potash and the mixture vigorously shaken in the corked flask five or ten minutes, when the eugenol will be dissolved. Water is then added till the floating stratum of non-phenolic constituents is brought into the neck of the flask, which should be warmed to assist in the separation of the unabsorbed caryophyllene. The liquid is finally cooled to 15° C., the insoluble oil measured, and the volume multiplied by 0.908 (the approximate specific gravity of caryophyllene). The weight of insoluble oil thus found is subtracted from the total weight of the oil used, the difference being the eugenol in the sample taken. The results are usually somewhat high owing to the slight solubility of the sesquiterpene in the alkaline liquid[1] and to the presence of esters in the oil, but by using 85 cc. of a

[1] E. C. Spurge states that a fair approximation to the result corrected for this solubility may be made by simply multiplying the volume of terpene found by 10 (using 10 cc. oil), this being considered the percentage of terpene in the oil.

solution of caustic potash of 5 per cent. strength, to 10 cc. of the sample, E. C. Spurge finds that better results are obtainable. Umney's method is accurate to within 2 per cent. if a correction is made for the presence of esters (determined by saponification), and it affords a valuable comparative test between various samples of oil, the result representing the total eugenol (free and as esters). The U. S. Pharmacopœia (8th Rev.) requires oil of cloves to contain at least 80 per cent. of eugenol, as shown by this process, using 5 per cent. potassium hydroxide solution.

In a method proposed by H. Thoms (*Ber.*, 1891, page 283; abst. *Analyst*, 1892, p. 11) the eugenol is weighed as its benzoyl-derivative. If the process be applied to the original oil, the amount found represents the free eugenol present, *plus* a variable proportion of eugenol esters. Thoms has, however, recently modified the process which, when the free eugenol only is to be determined, is carried out as follows:—A weight of 5 grammes of the oil is dissolved in ether and rapidly shaken out, first with about 20 cc. and then with another 5 cc. of 15 per cent. aqueous caustic soda solution. The mixed alkaline liquid is warmed to expel any dissolved ether, and the process then carried out as described below, the benzoyl chloride being added to the liquid.

When the oil is examined by Thoms' method *after saponification*, the result represents the total eugenol present (*Pharm. Zeit.*, 1903, p. 781; abst. *Analyst*, xxviii, p. 362). The oil is heated on the water-bath for a short time (30 minutes) with 20 cc. of a 15 per cent. aqueous solution of caustic soda. Alcoholic soda should not be employed, since the alcohol can only be completely removed with difficulty, and any remaining would affect the results by the formation of ethyl benzoate with benzoyl chloride. After saponification, the caryophyllene is separated from the alkaline liquid and washed twice with caustic soda solution, the washings being added to the alkaline liquid. This latter is then treated with 6 grammes of benzoyl chloride. The mixture is well stirred or vigorously shaken for a few minutes, when much heat is developed. The reaction is completed on the water-bath, and the uncombined benzoyl chloride is volatilised by the heat. On cooling the liquid, crystalline benzoyl-eugenol separates. Fifty cc. measure of water is now added, and the liquid warmed until the compound melts and collects as an oil. The mixture is well stirred, then cooled, and the clear supernatant liquid filtered from the crystals. The washing is repeated at least twice in this manner with 50 cc. of water (making 150 cc. in all), the washings being poured through the original filter. Any crystals which may have been carried over into the filter are returned to the beaker as far as possible, after which 25 cc. of hot alcohol (90 per cent. by weight) is poured through this filter to dissolve any small crystals which

may have remained behind, the alcohol being allowed to run into the beaker containing the moist benzoyl-eugenol. The liquid is warmed on the water-bath until solution is complete, when it is removed from the bath and stirred until the compound has separated in fine crystals. The liquid is then cooled to 17° C. The crystals are collected on a small tared filter, and washed with a little hot alcohol (90 per cent.) till the filtrate with the washings measures exactly 25 cc. The crystals are dried at 101° C. to constant weight. Thoms directs that a correction for the solubility of the benzoyl-derivative in 90 per cent. alcohol at 17° be made, 0.55 gramme being added to the weight of the dry benzoyl-eugenol.[1] The corrected weight in grammes of the compound, multiplied by the factor 0.6119, gives the grammes of total eugenol in the amount of the sample taken.[2]

The following method for the determination of free eugenol in essential oils has been proposed by Verley and Bölsing (*Ber.*, 1901, xxxiv, p. 3354). The process depends on the fact that acetic and other anhydrides react vigorously upon phenols and alcohols in presence of excess of pyridine, and in many cases the combination of phenol and acid anhydride is quantitative and practically instantaneous. Eugenol reacts readily, forming eugenyl acetate and acetic acid, the latter being taken up by the pyridine, and pyridine acetate produced. This latter compound reacts to phenolphthaleïn exactly like acetic acid, and can therefore be titrated, since pyridine is unaffected by this indicator. From one to two grammes of the sample to be examined is introduced into a flask of 200 cc. capacity, and 25 cc. of a mixture of acetic anhydride and pyridine added.[3] The whole is then heated for fifteen to thirty minutes on the water-bath (a condenser is unnecessary), the liquid cooled, 25 cc. of water added, and the mixture shaken. The acetic acid is then titrated with seminormal caustic alkali and phenolphthaleïn. A similar quantity

[1] E. C. Spurge finds that Thoms' correction, which was based upon experiments on pure eugenol in the absence of the sesquiterpene, gives results which are about 4 per cent. too low. The correction is best made by saponifying the benzoyl-eugenol dissolved in the alcoholic filtrate, and determining the compound by titration, the amount found being added to the weight of the crystals previously obtained.

[2] Or, since the molecular weights of eugenol and benzoyl-eugenol are 164 and 268 respectively, then if a be the weight of benzoyl-derivative and b the grammes of oil taken for analysis, the percentage of eugenol is found by the formula:—

$$\frac{164 \times (a + 0.55) \times 100}{268 \times b}$$

[3] The mixture is made up by mixing 30 grammes of acetic anhydride with 220 grammes of *absolute* pyridine. No reaction takes place, but on the addition of water the anhydride is decomposed with formation of pyridine acetate, which is easily saponified by alkali.

(25 cc.) of the pyridine and acetic anhydride mixture is diluted with hot water and titrated direct. The difference in the volume of alkali required for the two titrations, multiplied by 0.582, gives the eugenol in the amount of sample taken.

According to E. C. Spurge (*Pharm. Jour.*, 1903, ii, pp. 701, 757), none of the methods already described gives strictly accurate results. He considers Verley and Bölsing's method to be rapid and simple, yielding a determination of the free eugenol in clove oil within one per cent.[1] The combined eugenol should be determined by saponification. Spurge regards Thoms' method as tedious but capable of improvement, though he prefers the method of Verley and Bölsing, or that of Umney when modified as already described (page 361), and corrected for the presence of esters in the oil as determined by saponification.

ASAROL. (Asarone.) Propenyl-trimethoxy-benzene.

$$C_3H_5.C_6H_2(O.CH_3)_3$$

This body forms the solid constituent of the oil of European snake-root or hazel-wort (*Asarum Europæum*), and is also found in Matico oil. It crystallises in monoclinic prisms.

By the action of potassium permanganate, asarol is oxidised to *asarylic* (trimethoxy-benzoic) *acid*, melting at 144°. With bromine, asarol yields a crystalline dibromide, melting at 85° to 86° C.

APIOL. Allyl-tetrahydroxybenzene dimethyl-methylene ether.

$$C_3H_5.C_6H(OCH_3)_2:O_2:CH_2$$

This compound, sometimes termed parsley-camphor, occurs in oil of parsley (from *Petroselinum sativum*), in which it is present to the extent of about 20 per cent. An isomer of this body, termed dill-apiol, occurs in oil of dill.

Apiol may be extracted from the seeds of the parsley plant by treating them with alcohol, and then extracting the residue with ether. Apiol crystallises from the ethereal solution on evaporation in long colourless needles, having a faint odour of parsley.

Apiol is insoluble in water, but is very soluble in alcohol, ether, and in fixed and volatile oils. It does not combine with bases or acids, and does not react with hydroxylamine or phenylhydrazine.

[1] Schimmel & Co. (*Report*, April, 1903), however, state that the method is unreliable, but their opinion is chiefly based upon the fact that Umney's method gave in their hands higher results on certain samples of clove oil than that of Verley and Bölsing. It has, however, been shown that Umney's method, when uncorrected, invariably gives high results in the case of clove oil (page 361).

When treated with oxidising agents, apiol is converted into *apiolaldehyde*, $C_{10}H_{10}O_5$, a small quantity of a volatile acid being simultaneously formed; and by prolonged treatment with potassium permanganate yields *apiolic acid*, $C_{10}H_{10}O_6$.

On boiling apiol with alcoholic potash, it is converted into *iso-apiol.*

By the action of fuming nitric acid (sp. gr. 1.48) apiol is oxidised to oxalic acid and a crystalline golden-yellow nitro-compound, melting at 116°. By the action of bromine on a solution of apiol in carbon disulphide, *tribromapiol*, $C_{12}H_{11}Br_3O_4$, is formed, and is obtained by crystallisation from alcohol in flat needles melting at 88°. Tribromapiol dissolves in concentrated sulphuric acid with violet colour.

Commercial apiol is an oily green liquid, containing a large proportion of true apiol. It varies considerably in density, colour, action of solvents, and heat. Pure apiol is volatilised unchanged by heat, but many commercial specimens are decomposed. The specific gravity of apiol, according to the Belgian Pharmacopœia, is 1.07 to 1.08. French apiol has a much lower specific gravity.[1]

DIOSPHENOL. $C_{10}H_{16}O_2$; or, $C_9H_{14}(OH).COH$ (See page 251.)

Diosphenol is a colourless crystalline substance boiling at 112° under 14 mm. pressure, and at 232° at ordinary atmospheric pressure. It is optically inactive.

Diosphenol has at once the properties of a phenol and an aldehyde. It forms an oxime and a hydrazone. (See Semmler, *Ber.*, 1906, p. 1158). Diosphenol may be extracted from oil of buchu by caustic potash, and is precipitated from the solution by acids. It gives a dark green coloration with ferric chloride.

A. C. Chapman (*Analyst*, 1900, page 313) has described the following simple colour-reactions for distinguishing between certain of these isomeric allyl- and propenyl-phenols. One cc. of the highly-purified phenol is dissolved in about 5 cc. of acetic anhydride, and to the solution thus obtained (*a*) a small fragment of fused zinc chloride, or (*b*) one drop of strong sulphuric acid, is added:—

	EUGENOL.	ISO-EUGENOL.
H_2SO_4	Brown at first, becoming quickly purple, and finally wine-red.	A rose pink, quickly changing to a light brown.
$ZnCl_2$	Pale yellow, the colour disappearing on standing.	Bright rose-pink coloration.

[1] The sinking of apiol in water is valueless as a test for the presence of impurities, since a sample mixed with an equal volume of olive oil behaves exactly as pure apiol in this respect.

	SAFROL.	ISO-SAFROL.
H_2SO_4,	A bright emerald-green colour, becoming brownish-green and finally brownish.	A faint transient pink, becoming reddish on standing.
$ZnCl_2$,	Pale blue, becoming less intense on standing, and finally light brown.	Pink, becoming brownish-pink and finally brown.

	ESTRAGOL.	ANETHOL.
H_2SO_4,	Purple, turning to indigo blue, and then to bluish purple.	No colour at first. After a short time a yellowish tinge.
$ZnCl_2$,	Blue-violet colour, which becomes deep mauve and finally brownish.	A pale yellow colour appearing slowly, which deepens on standing, and finally becomes brick-red.

KETONES OF ESSENTIAL OILS.

Compounds of ketonic functions occur in essential oils more commonly than was recognised till recently. They may be mostly classified as *camphoroids; thujone* and its isomers; *carvone* and its allies; and *open-chain ketones*, such as methyl-heptenone and methyl-nonyl ketone.[1] Menthone is described on page 350.

Camphoroids.

Many essential oils contain oxygenated bodies which are frequently grouped together under the common name of "camphors." These compounds, with a few exceptions (*e. g.*, the

[1] METHYL-HEPTENONE, $CH_3.C(CH_3):CH.CH_2.CH_2.CO.CH_3$ (see page 252), exists ready-formed in lemon-grass oil to the extent of 1 to 4 per cent. For its extraction, the fraction of the oil distilling at 180° should be agitated with a solution of sodium bisulphite in 1½ parts of water. The ketone liberated from the solid bisulphite compound on treatment with soda is optically inactive, has a refractive index of 1.43805 at 20°, and yields a semicarbazone melting at 134°. Methyl-heptenone also results from the distillation of cineolic anhydride.

METHYL-NONYL-KETONE, $CH_3.CO.C_9H_{19}$, *occurs in oil of rue to the* extent of about 90 per cent. It is a liquid of pungent odour, which solidifies when strongly cooled, melts at 13°, and boils at 225° C.

Irone, $C_{13}H_{20}O$, is a ketone possessing an odour of violets in alcoholic solution, and is contained in dried orris root (iris root), from which Tiemann and Krüger extracted it in the form of an insoluble dextro-rotatory oily body of spec. gravity 0.939 at 20° C., and boiling at 144° at 16 mm. pressure.

Irone is a cyclic methyl ketone of the formula:—

$$(CH_3)_2.C\left\langle\begin{array}{l}CH(CH:CH.CO.CH_3).CH.CH_3\\CH:CH\text{——————————}\end{array}\right\rangle CH_2.$$

It is isomeric with the synthetic "ionones" prepared from citral (p. 392).

paraffin of rose oil), form the so-called *stearoptenes* of essential oils. They are solid at the ordinary temperature, crystallisable, volatile, and nearly insoluble in water or aqueous solutions of alkalies or acids.

While possessing very similar physical properties, these camphoroid bodies are of somewhat varied chemical constitution. Some of them, as *borneol*, have the constitution of alcohols; others, as *apiol* (the camphoroid of parsley oil), are phenolic ethers; while others, as common *camphor*, are of ketonic character. Some of the camphoroids have the same ultimate composition as common camphor and its physical isomerides. Others, as *matico-camphor*,[1] have the composition of homologues of laurel-camphor. *Cedrol* and other compounds of the formula $C_{15}H_{26}O$ are sometimes designated *sesqui-camphors*, but really have the constitution of sesquiterpene alcohols (page 353).

It is very desirable to restrict the use of the term "camphor" to laurel camphor and its immediate analogues of ketonic character.

LAUREL CAMPHOR. JAPAN CAMPHOR. $C_{10}H_{16}O$; or, $C_8H_{14}\left\{\begin{matrix}CO\\CH_2\end{matrix}\right\}$

Common or Japan camphor occurs in minute crystals in the wood of the camphor-laurel (*Laurus* or *Cinnamomum camphora*), and is extracted by distilling the chopped-up branches of the tree with water.[2]

Camphor also occurs in the oils of sage, lavender, spike-

[1] MATICO-CAMPHOR, $C_{12}H_{20}O$, occurs in the essential oil obtained from the leaves of the narrow-leaved pepper (*Piper angustifolium*) of South America, which are employed locally for small wounds, such as leech-bites. After purification from admixed resins by repeated crystallisation, the camphor forms hexagonal crystals, is colourless and odourless, melts at 94°, and gyrates like common camphor when thrown on to water. Matico-camphor is not attacked by aqueous alkalies, but is readily soluble in alcohol, ether, chloroform, benzene, and petroleum spirit.

According to K. Kügler (*Ber.*, xvi, 2841), in contact with hydrochloric acid matico-camphor assumes an intense violet colour, which changes to blue and then to green, and on extraction with ether a compound is obtained which forms brown crystals and exhibits a green fluorescence. With strong sulphuric acid, matico-camphor becomes yellow, then red, and finally violet. With a mixture of sulphuric and nitric acids it assumes a yellow colour, changing to violet and finally to blue.

[2] The crude camphor thus obtained is exported from Japan and Formosa, and to a limited extent from China, and is refined in Europe by mixing it with a small proportion of lime or charcoal and subliming it in large glass vessels called "bombolas." In Britain and America, camphor is now frequently purified by subliming it from iron retorts into a cooled chamber, where it condenses in the form of flowers of camphor. It is subsequently pressed into transparent cakes by hydraulic power.

Details of the process of camphor distillation have been published by H. Oishi (*Chem. News*, 1884, i, 275). D. Hooper has described the hahitat and growth of the camphor-tree (see *Pharm. Jour.*, Jan. 11, 1896).

lavender and rosemary. It results from the oxidation of borneol by nitric acid, and is a product of the oxidation of camphene by platinum-black or chromic acid mixture.[1] Camphor is also formed by distilling a mixture of calcium camphate and formate.

Camphor occurs in commerce in colourless, translucent, tough, fibrous masses; in transparent rectangular tablets; and in a pulverulent form known as "flowers of camphor." Camphor may also be obtained crystallised in hexagonal prisms terminated by hexagonal pyramids.

Camphor has a peculiar fragrant odour and somewhat bitter, burning taste, followed by a sensation of cold. It is very readily inflammable, burning with a bright but very smoky flame. Camphor vapourises rapidly at ordinary temperatures, and is often found deposited in minute but very perfectly-formed crystals on the sides of the bottles in which it is preserved. Camphor sublimes without residue when heated. It melts at 175° C., and at 204° boils and distils unchanged.[2]

Ordinary or laurel camphor is dextro-rotatory, the apparent specific rotation varying with the nature of the solvent and the concentration of the solution.[3] Landolt gives the formula:—

$$[a]_D = +55.4° - (a \times q);$$

where q is the number of grammes of solvent in 100 grammes of the solution. The value of a varies with the solvent, being

[1] Nordheim has patented a process for the manufacture of artificial camphor which is based on the treatment of dextro-pinene with chlorine. The solid product is purified from liquid isomers in the ordinary manner, decomposed by sodium carbonate, and heated to 120°. The camphene which volatilises is oxidised to camphor by ozonised air.

Camphor has been prepared synthetically by the action of anhydrous oxalic acid upon anhydrous turpentine oil at 120° to 130°. Camphor, borneol, bornyl esters, and polymerisation products are produced. The bornyl esters are separated by the action of caustic lime, and the impurities removed by subsequent distillation. The borneol is then oxidised to camphor by the action of chromic acid mixture.

Other methods for the artificial production of true camphor are those based (1) upon the conversion of pinene mono-hydrochloride into camphene by heating with an alkali and sodium acetate, and the subsequent oxidation of the camphene into camphor by potassium permanganate; (2) on the formation of camphoric acid by the prolonged action of hot air and water on oil of turpentine, and reduction of the camphoric acid to camphor by nascent hydrogen. (See also Marsh and Stockdale, *Jour. Chem. Soc.*, 1890, lvii, 961.)

[2] According to F. Foerster, carefully purified camphor melts at 209.1°.

[3] The essential oil obtained by distillation from the leaves of feverfew (*Matricaria parthenium*) contains a variety of camphor agreeing in all respects with that obtained from the camphor-tree except that it exhibits a left-handed rotation equal to the dextro-rotation of the latter kind. By mixing these two varieties of camphor in equal proportions, a *racemoid camphor* is obtained which is optically neutral. This inactive camphor melts at 179°, and yields derivatives which differ in their solubilities and melting-points from the parallel products obtained from ordinary camphor. (See A. Haller, *Compt. rend.*, cv, 66.) A camphor which appears to differ from laurel-camphor merely in being optically inactive

0.1372 for alcohol and 0.1632 for benzene. Thus the apparent specific rotatory power of a solution of 10 grammes of camphor in 90 grammes of alcohol will be:—

$$+55.4° - 12.348° = +43.052°.$$ [1]

The *following determinations of the specific rotation of* camphor when dissolved in fixed oils are by P. Chabot (*Compt. rend.*, cxi, 231):—

	Olive Oil.	Almond Oil.	Grape-seed Oil.
$[\alpha]_D$ in 3 per cent. solution, . .	55.7°	56.8°	54.4°
$[\alpha]_D$ in 20 per cent. solution, .	55.2°	54.3°	54.3°

is contained in the fraction of oil of sage distilling between 205° and 208°. According to Montgolfier, when a camphor is reduced to borneol the rotation of the latter varies with each operation, but the camphor regenerated by oxidising the borneol has always the rotatory power of the original camphor. (See also A. Haller, *Compt. rend.*, cv, 227.)

[1] From the observations of Partheil and van Haaren (*J. S. C. I.*, 1900, p. 684) it appears that the more dilute the alcohol, the lower the apparent specific rotation of the dissolved camphor. Hence the amount of the latter cannot be accurately deduced from the observed rotation, unless *the strength of the alcohol be also known. Further, when the solvent* is kept of constant strength the specific rotation decreases slightly as the percentage of camphor increases. Partheil and van Haaren propose the formula: $P = 1.5152\,a$, where P is the percentage of camphor by weight and a the observed rotation for 200 millimetres. To ascertain the specific gravity of the alcohol used (S), they propose the following formula:

$$S = \frac{100 - p}{\frac{100}{d} - 1.05\,p};$$ where p is the percentage of camphor by weight and d the specific gravity of the camphorated spirit. Partheil and van Haaren give the following table:—

No.	Sp. Gr. of Alcohol Used.	Camphor, Per Cent.	Observed Rotation, 200 mm.	Specific Rotation, $[\alpha]_D$.
1, ...	0.7896	10	6.98°	43.4362
2, ...	0.8212	10	6.78°	40.6666
3, ...	0.8505	10	6.69°	39.0439
4, ...	0.8637	10	6.65°	38.1439
5, ...	0.8781	10	6.60°	37.2755
6, ...	0.8909	10	6.59°	36.7622
7, ...	0.9007	10	6.59°	36.4008
1, ...	0.7895	8.37	5.79°	43.2142
2, ...	0.7895	6.81	4.69°	43.1411
3, ...	0.9007	8.35	5.48°	36.2929
4, ...	0.9007	6.82	4.40°	35.6951

From these results it appears that the value of $[\alpha]_D$ varies little, but somewhat increases, with the dilution, whereas the reverse is the case with solutions of camphor in alcohol and benzene. (See also Leonard and Smith, page 372.)

Camphor is somewhat lighter than water, having a specific gravity which is given variously from 0.980 to 0.996. When thrown on the surface of clean water, camphor goes through rapid whirling movements, which are arrested by the addition of a drop of oil.

Camphor is only very sparingly soluble in water (1 : 1000) and not more soluble in dilute alkalies or acids.[1] It dissolves in less than its own weight of alcohol (120 : 100) of 0.806 specific gravity, and is readily soluble in ether, chloroform, acetone, glacial acetic acid, carbon disulphide, and fixed oils. A saturated solution of camphor in olive oil contains 27 per cent. by weight of camphor.

Camphor Water, B. P. (1898), is a 0.1 per cent. solution of camphor, and is directed to be prepared by dissolving 1 part by weight of camphor in sufficient alcohol (90 per cent.) to form 3 measures, and then pouring the solution gradually with shaking into 1000 parts of water, the liquid being occasionally shaken until the camphor is dissolved. The solution has an extensive use in medicine.

Spirit of Camphor, B. P. (1898), is a solution of 1 part of camphor in 9 of 90 per cent. alcohol. The corresponding preparation of the United States Pharmacopœia (8th Rev.) is made by dissolving 100 grammes of camphor in sufficient alcohol to form 1 litre. The author has observed that such a solution occupies fully the volume of the spirit used *plus* that of the camphor before solution, there being slight expansion rather than contraction in the process of solution. Rubini's "Essence of Camphor" (*Spiritus camphoræ fortior*) is a solution of camphor in an equal weight of rectified spirit.

On diluting an alcoholic solution of camphor with water, the solid is precipitated in white flocks. If the proportion of alcohol exceeds a certain limit, no amount of dilution will effect precipitation of the camphor.

Liniment of Camphor or *Camphorated Oil*, B. P. (1898), is a solution of one part by weight of camphor (in flowers) in four parts by measure of olive oil. Hence the preparation, when properly made, contains almost exactly 21 per cent. by weight of camphor.[2] The corresponding preparation of the United States

[1] Istrati and Zaharia (*Compt. rend.*, 1898, cxxvii [16], 557) find a saturated solution of camphor in water at 15° C. to have a specific gravity of 1.00071, and to exhibit a rotation of +0.4°. They state that camphor is readily soluble at 0° in hydrochloric acid, and that on warming this solution a white substance separates out which redissolves on cooling.

[2] The author has proved that no loss of camphor occurs in the preparation of the liniment if reasonable care is exercised.

Pharmacopœia (8th Rev.) is a solution of one part of camphor in four of cottonseed oil.[1]

When camphor is triturated or heated with menthol, thymol, phenol or chloral hydrate the mixture speedily liquefies. The products, which appear to be definite compounds, have received a limited application in medicine.

Camphor absorbs hydrochloric acid, nitric peroxide, and sulphur dioxide gases, forming colourless liquids which are decomposed on addition of water. The compound of camphor with sulphur dioxide has been proposed as a disinfectant under the name of "Thiocamph."

Camphor is extensively employed in medicine, both internally and externally. In large doses it is distinctly poisonous, the most marked symptoms being cardiac depression, lividity of countenance, convulsions, stupor, retention of urine, and, in extreme cases, collapse. When ingested by the dog, camphor appears in the urine as *campho-glycuronic acid,* $C_{16}H_{24}O_8$, which when boiled with dilute hydrochloric acid yields *camphorol,* $C_{10}H_{16}O_2$, a body which crystallises in thin tablets, melts at 197° to 198°, sublimes readily, and yields camphoric acid on oxidation.

Camphor has distinct, but not very powerful, antiseptic properties, and is inimical to insect-life. Hence its employment for preserving animal specimens iu museums, &c.

Camphor is used extensively for the manufacture of the nitrocellulose products known as *celluloid* and *xylonite,* and is or was an ingredient of some varieties of blasting gelatin and smokeless powder.

Determination of Camphor.—Camphor can be readily separated from non-volatile substances by distilling the mixture in a current of steam, but its accurate determination in presence of other volatile bodies presents some difficulty. The proportion of camphor present in camphor liniment (page 370) and similar preparations can be ascertained with considerable accuracy by the direct observation of the optical activity of the liquid.

The following figures by N. Leonard and H. M. Smith (*Analyst,* 1900, p. 202) show the optical activity of solutions of various

[1] Numerous samples of "Camphorated Oil" purchased in the West Riding of Yorkshire under the provisions of the Sale of Food and Drugs Act, were found to contain various proportions of camphor from 21 per cent. down to less than 1 per cent., from 3 to 5 per cent. being quite common. Cottonseed and sesame oils were in some cases substituted for olive oil, and the vegetable oils were not unfrequently partly or wholly replaced by heavy mineral oil. Methods for the detection of the various vegetable oils will be found in Vol. II, Pt. i. There is no foundation for the statement frequently made in defence that the camphor readily volatilises from the solution.

strengths of camphor in olive oil. Line 4 in the table shows the observed angular rotation of the solution in a 200 mm. tube. Line 5 shows the calculated angular rotation for 1 per cent. of dissolved camphor. These latter figures are corrected for the small rotation of olive oil itself, which, according to Bishop (*J. S. C. I.*, 1887, p. 750), is +0.13° for 200 mm. Line 6 which has been added by the author, shows the apparent specific rotation of camphor calculated from Leonard and Smith's data.[1]

	A.	B.	C.	D.
1. Dissolved Camphor, per cent.,	5.32	11.26	20.66	26.78
2. Specific gravity at 60° F.,	0.91903	0.92173	0.92604	0.92911
3. Rise of Sp. gravity for 1 % camphor,	0.000446	0.000450	0.000454	0.000465
4. Angular rotation per 200 mm.,	5.26°	11.35°	20.74°	26.79°
5. Angular rotation for 1 % camphor,	0.964°	0.998°	0.998°	0.996°
6. Apparent Spec. rotation of dissolved camphor,	52.4°	54.0°	53.9°	53.6°

It will be seen from these results that the rotation of the liquid is increased by nearly 1° for each unit per cent. of camphor present, and that the observed angular rotation of a sample of camphorated oil in a 200-millimetre tube gives at once, without calculation, the percentage of camphor with sufficient accuracy for most purposes. The rotation appears not to be appreciably influenced by ordinary variations of temperature.[2]

For the gravimetric determination of camphor in camphor liniment, 5 grammes of the sample should be heated in a shallow capsule to 120° for about two hours, when the loss of weight will

[1] Leonard and Smith found the rotation of two specimens of rape oil to be —0°.16 and —0°.3, and of sesame oil +1°.6, per 200 mm., results which are in accord with those of Bishop, whilst two samples of fluorescent mineral oil gave them rotations of + 0°.12 and + 0°.42. Experiments with rape oil and mineral oil showed, however, that the increased rotation caused by the solution of camphor in these oils is practically the same as with olive oil, so that if the nature of the oil used in the preparation of the sample is known, the process is still applicable. For the identification of the oil used, they found that the sample could be examined directly with the refractometer, the refractive index of the oil being apparently almost unaffected by the presence of dissolved camphor.

[2] *D was a saturated solution prepared by gently warming olive oil* with excess of camphor, cooling to about 10° C., and filtering. The contained camphor was then ascertained from the loss of weight sustained no heating a portion of the solution at 110° to 120°.

be that of the camphor volatilised.[1] Or a good plan is to heat the liquid in a capsule over a water-bath, when the greater portion of the camphor will readily be volatilised and the remainder can be removed in the air-bath as before (Tankard). The same method will give fairly good results with samples containing heavy mineral oil, but in the case of a more volatile fraction of petroleum being present the loss of weight will, of course, not be due solely to the camphor. F. Foerster drives a current of open steam through the oil, and when the distillate amounts to about 300 cc. redistils it with the addition of a little alkali and a spiral of platinum wire to prevent bumping. The distillate is agitated with benzene and the amount of camphor deduced from the optical activity of the liquid. (See page 368).

F. Foerster (*Ber.*, xxiii, 2981; abst. *J. S. C. I.*, ix, 1159) employs a similar process for the determination of the camphor in celluloid, xylonite, ivorine, and similar preparations. For this purpose, a quantity of the sample containing from two to three grammes of camphor is treated in a flask furnished with a condenser and tapped funnel with sufficient of a 10 per cent. solution of caustic soda to saponify the substance. The flask is heated to about 80° C. till saponification is complete, when sufficient concentrated alkali is added to raise the strength of the liquid in the flask to about 10 per cent. of NaHO. The contents of the flask are then diluted, if necessary, to about 250 cc., and distilled till about half the volume has passed over. The condenser should be connected air-tight with the receiver, which should have a second orifice fitted with a U-tube containing an exact measure of benzene, to catch any uncondensed camphor-vapour.[2] When the distillation is complete, this benzene is added to the contents of the condenser, and more added to bring the total volume employed to 25 cc. The contents of the receiver are then agitated to dissolve the camphor in the benzene, the latter separated from the water, brought to a temperature of 20° C., and the optical activity observed with a polarimeter. According to Foerster, the specific rotation of camphor in benzene solution is $+39.755° +0.17254\ t$, whence $[\alpha]_D = +40.11°$ at 20° C. (Compare Landolt's formula on page 368.)

[1] Some samples of olive oil appear to gain slightly in weight on heating, while others lose weight. (See A. W. Nunn, *Pharm. Journ.*, 1902, lxix, 106.) It has been proposed to make a correction for this change, but this refinement is unnecessary.

An indirect method of determining camphor in the liniment (in the absence of mineral oil) consists in applying Koettstorfer's saponification process. The weight of potassium hydroxide (KHO) required for the saponification, multiplied by 5, gives the weight of fatty oil present in the portion of the sample operated on. Five grammes is a suitable quantity of oil to employ. The results are satisfactory.

[2] Foerster uses a special form of receiver.

From *alcohol*, camphor may be partially separated by addition of water (see above), the solution being afterwards fractionally distilled. Or the camphor may be extracted from the largely diluted liquid by agitating it with a known weight or measure of petroleum, and its amount deduced from the increased weight or volume of the separated solvent. O. Schmatolla agitates 10 grammes of the spirit in a burette with about 30 cc. of a saturated solution of common salt, and dissolves the precipitated camphor by adding exactly 1 cc. of petroleum and gently rotating the burette. The increase of volume of the petroleum is noted, each 1.02 cc. representing one gramme of camphor.

When the proportion of camphor in an alcoholic solution is roughly known, the amount may be deduced from the optical activity of the liquid, but the result will be only approximate unless the strength of the alcohol be also known. (See pages 368, 369.)

Bromocamphor. $C_{10}H_{15}BrO$. Camphor unites with bromine to form the additive-compound, $C_{10}H_{16}O,Br_2$, which readily decomposes yielding bromocamphor.[1] For the preparation of the latter, 30 parts of camphor and 32 of bromine should be dissolved in 18 of chloroform. After standing a few hours, the solvent should be distilled off, the residue washed slightly with alcohol, and recrystallised from ether. Bromocamphor forms prismatic scales or needles having an odour and taste resembling camphor. It melts at 76° and sublimes at a somewhat higher temperature. At 274° it boils and distils unchanged, leaving no residue. Bromocamphor is nearly insoluble in water, sparingly soluble in glycerin, moderately (1 : 8) in olive oil and 90 per cent. alcohol (1 : 12), and readily soluble in ether, chloroform and benzene.

When boiled with a solution of silver nitrate, bromocamphor is decomposed, a precipitate of silver bromide being formed. Bromocamphor is soluble without decomposition in cold concentrated sulphuric acid, and is precipitated unaltered when the solution is poured into excess of water. When treated in alcoholic solution with caustic potash or sodium amalgam, bromocamphor is reduced to camphor. When treated with sodium in toluene solution, it yields sodium-camphor.

Bromocamphor is employed in medicine as a sedative and hypnotic, and has been found specially useful in cases of hysteria, dipsomania, and delirium tremens. It is official in the United States Pharmacopœia, and in most others except the British.

[1] *Dibromocamphor*, $C_{10}H_{14}Br_2O$, is obtained by the action of bromine on monobromcamphor. Two modifications exist, the *alpha*-variety melting at 61° and volatilising readily with steam, while the *beta*-modification melts at 115° and is only slightly volatile in a current of steam.

Nitro-bromocamphor, $C_{10}H_{14}Br(NO_2)O$, is formed by the action of strong nitric acid on bromo-camphor. It crystallises from its solution in boiling alcohol in long needles which melt at 104° to 105°. It is very sparingly soluble in cold alcohol and is insoluble in alkalies.

Nitrocamphor, $C_{10}H_{15}(NO_2)O$, is obtained by treating nitro-bromocamphor with alcoholic potash, or by the action of a copper-zinc couple on its boiling alcoholic solution. The resultant zinc salt, which crystallises readily, is decomposed by hydrochloric acid. The nitrocamphor which separates may be shaken out with benzene.[1]

Amidocamphor, $C_{10}H_{15}(NH_2)O$, is produced when nitrocamphor is dissolved in a strong solution of caustic potash and treated with sodium-amalgam. It is a viscid liquid of strongly alkaline reaction, boils at 246°, has a strong ammoniacal odour, and forms a crystalline hydrochloride.

Camphoroxime, $C_{10}H_{16}NOH$, is formed when a solution of camphor in alcohol is treated with a concentrated aqueous solution of hydroxylamine hydrochloride, sodium carbonate added till the liquid is alkaline to litmus, and the solution diluted with alcohol and allowed to stand for eight days. The liquid is then largely diluted with water, when the camphoroxime is precipitated; or the alcohol may be removed by evaporation and the residue extracted with ether. On evaporation of its ethereal solution camphoroxime crystallises in white needles, but from alcohol it separates in transparent sword-shaped prisms, which have an odour like camphor and gyrate on water. Camphoroxime melts at 118°, and boils with slight decomposition at 249°. It is nearly insoluble in water, but dissolves in alcohol, ether, solutions of caustic alkalies, and acids. *Camphoroxime hydrochloride* is a voluminous white powder, which is but sparingly soluble in water, but dissolves readily in alcohol and in acids. The formation of camphoroxime may be utilised for the detection of camphor.

Camphor does not react with acetyl chloride and forms no compound with alkali-metal bisulphites.

[1] By crystallising the product from alcohol, it may be separated into two isomers. The *alpha*-compound is less soluble in cold alcohol than the isomer. It forms trimetric prisms, melting at 101°. The β-nitrocamphor forms fern-like crystals which melt at 98°. Both modifications have strongly marked acid properties, redden litmus, and decompose carbonates. In the free state, the nitrocamphors are lævo-rotatory, but their salts are dextro-rotatory. They evolve an odour of myrrh when heated. The salts of the alkali-metals and magnesium, and the β-*salt of zinc are* soluble in water. The *copper salt*, $[C_{10}H_{14}(NO_2)O]_2Cu + H_2O$, is a chestnut-brown precipitate, soluble in alcohol to a brown solution, from which it separates in small, grass-green crystals. The *ferrous salt* forms tablets of a garnet-red colour, while the *ferric salt* is a blood-red precipitate, soluble in alcohol with deep red colour.

Camphor is not affected by the ordinary reducing agents, but if dissolved in an inert liquid, such as toluene, and heated to 90° with metallic sodium, it forms *sodium-camphor*, $C_{10}H_{15}.ONa$, and *borneol*, $C_{10}H_{18}O$, thus behaving as a phenol. By distillation with zinc chloride or phosphoric anhydride camphor yields cymene, water, and other products, while *carvacrol* is produced by heating camphor with half its weight of iodine.

By boiling with alcoholic potash, camphor is said to yield borneol and *camphic acid*, $C_{10}H_{16}O_2$, a reaction which suggests an analogy to benzoic aldehyde, which under similar treatment gives benzyl alcohol and benzoic acid. When camphor vapour is passed over soda-lime heated to 400° *campholic acid*, $C_{10}H_{18}O_2$, is formed. The same product is obtained, together with sodium-camphor and sodium bornylate, when metallic sodium is added to a boiling solution of camphor in benzene. The mass is treated with water, and extracted with ether. The aqueous solution is then acidified with hydrochloric acid, and the campholic acid steam-distilled.

The action of oxidising agents on camphor has been the subject of much research, and the products have great theoretical interest. By prolonged treatment with nitric acid of 1.37 specific gravity, camphor is chiefly converted into *camphoric acid*, $C_{10}H_{16}O_4$,[1] which on further boiling is converted into *camphoronic acid*, $C_9H_{14}O_6$.[2] Camphoric acid is also the chief

[1] CAMPHORIC ACID, $C_8H_{14}(CO.OH)_2$, forms monoclinic crystals which melt at 186°, and at a somewhat higher temperature lose water, with conversion into *camphoric anhydride*, $C_{10}H_{14}O_3$, melting at 217°. Camphoric acid dissolves in 160 parts of cold water or in 10 parts at the boiling-point, and is readily soluble in alcohol, ether, and fixed oils. It is employed in medicine for the treatment of urinary calculi and vesical catarrh. A 1 per cent. solution has been recommended in acute and chronic affections of the respiratory passages. The camphorates are mostly insoluble, or nearly so. *Calcium camphorate*, $CaC_{10}H_{14}O_4 + 9H_2O$, forms fairly soluble crystals. Camphoric acid as ordinarily prepared is dextro-rotatory ($[\alpha]_D = +46°$), but a lævo-rotatory modification can be obtained by the oxidation of lævo-camphor. The two varieties combine to form an inactive racemoid camphoric acid which melts at 204°, and is less soluble than its isomerides. Inactive camphoric acid may also be obtained by oxidising inactive camphor at 100° by nitric acid.

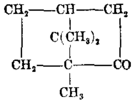
All six of the possible modifications of camphoric acid are known. Their constitution has been the subject of much study, and the synthesis of *r*-camphoric acid by G. Komppa in 1903 (*Ber.*, xxxvi, 4332) marks the conclusion of an important stage in camphor research, since this synthesis settles finally the vexed question of the constitution of camphor. (See page 377). Those interested in current lines of thought on the subject may consult recent papers in the *J. C. S.*, lviii, 517; lxii, 865, 1040, 1100; lxix, pp. 57, 90, 757; lxxi, p. 956; lxxiii, i, 68; lxxv, 986; lxxvii, 442, 536, 925–928; lxxviii, 182; lxxix, 110, 332, 1284; lxxxi, 18, 269, 549, 867, 1441; lxxxiii, 479, 835, 953; lxxxv, 128, 892, 1210; lxxxvii, 232, 722, 828, etc.

[2] CAMPHORONIC ACID, or isopropyl-carballylic acid, $C_6H_{11}(COOH)_3$, is obtained from the mother-liquors from which camphoric acid has been

product of the oxidation of camphor by potassium permanganate in the presence of caustic alkali; neutral permanganate has but little action on camphor. Dilute chromic acid mixture acts with difficulty on camphor, but by prolonged treatment camphoronic and hydroxy-camphoronic acids are produced.

The constitution of camphor has been the subject of much research and controversy, but has now been decided by the synthesis of *r*-camphoric acid by G. Komppa (1903). Since camphoric acid is convertible into homo-camphoric acid and the barium salt of homo-camphoric acid yields camphor upon distillation (Haller), the synthesis of camphor is complete. Komppa's results confirm the accuracy of J. Bredt's formula (1893), which has long been regarded as having the best claim of the 33 proposed formulæ for camphor. (See *Ann. Report, Chem. Soc.*, 1904, page 112.)

The following formula thus represents the constitution of camphor:—



J Bredt (1893).

The following formulæ may be regarded as fairly well established:—

CAMPHOR. $C_8H_{14}\begin{cases} CO \\ | \\ CH_2 \end{cases}$

BORNEOL. $C_8H_{14}\begin{cases} CH.OH \\ | \\ CH_2 \end{cases}$

HYDROXYCAMPHOR. $C_8H_{14}\begin{cases} CO \\ | \\ CH.OH \end{cases}$

CAMPHO-PHENOL. $C_8H_{14}\begin{cases} C.OH \\ \| \\ CH \end{cases}$

BROMOCAMPHOR. $C_8H_{14}\begin{cases} C.OBr \\ \| \\ CH \end{cases}$

NITROBROMOCAMPHOR. $C_8H_{14}\begin{cases} C.OBr \\ \| \\ C.NO_2 \end{cases}$

NITROCAMPHOL. $C_8H_{14}\begin{cases} C.OH \\ \| \\ C.NO_2 \end{cases}$

AMIDOCAMPHOR. $C_8H_{14}\begin{cases} C.OH \\ \| \\ C.NH_2 \end{cases}$

CAMPHOLIC ACID. $C_8H_{14}\begin{cases} CO.OH \\ CH_3 \end{cases}$

CAMPHORIC ACID. $C_8H_{14}\begin{cases} CO.OH \\ CO.OH \end{cases}$

CAMPHOROXIME. $C_8H_{14}\begin{cases} C:NOH \\ | \\ CH_2 \end{cases}$

ISOCAMPHOXIME. $C_8H_{14}\begin{cases} CO \\ | \\ CH.NH_2 \end{cases}$

separated. *It crystallises in bundles of needles* which melt at 139° and are very soluble in water, alcohol, and hydrous ether.

Thujone and its Allies.

Thujone, pulegone, and fenchone are ketonoid bodies present in certain essential oils. They are isomeric with camphor, $C_{10}H_{16}O$, but are distinguished by their low melting-points, being liquid at ordinary temperatures. The following table exhibits *their leading characters*:—

	FENCHONE.	PULEGONE.	THUJONE.
Chief sources,	Oils of fennel and thuja.	Oil of Penny-royal.	Thuja Oil.
Specific gravity,	0.9465 at 19°	...	0.9126 at 20
Refractive index,	1.4631 at 19°	1.4868 at 20°	1.4495
Specific rotation,	{ +71.8° / −66.9°	+22.9°	+68° [1]
Melting-point,	+5°	liquid	...
Boiling-point,	192° to 193°	221° to 222°	203°
Alcohol, $C_{10}H_{17}.OH$:—			
Melting-point,	40° to 41°	...	...
Boiling-point,	201°	103° at 15 mm. 215° at 760 mm.	93° at 13 mm.
Specific gravity,	0.933 at 50°	0.912 at 20°	0.9249 at 20°
Specific rotation,	±10.36°	...	...
Oxime, $C_{10}H_{16}:N.OH$:—			
Melting-point,	148° to 149°	118° to 119°	55°
Bisulphite compound,	none	crystalline	crystalline

FENCHONE. $C_{10}H_{16}O$ (See page 252.)

At ordinary temperatures fenchone is a colourless liquid of camphoraceous odour. It does not react with phenyl-hydrazine or sodium bisulphite (distinction from pulegone and thujone). When fenchone in alcoholic solution is treated with sodium, it is reduced to *fenchyl alcohol*, $C_{10}H_{17}OH$, a colourless crystalline body. The alcohol derived from dextro-fenchene is lævo-rotatory, while that from lævo-fenchene exhibits equal dextro-rotation. On oxidation, fenchyl alcohol is converted into a fenchone of opposite rotation. On treatment with phosphorus pentachloride, fenchyl alcohol yields *fenchyl chloride*, $C_{10}H_{16}Cl$, which is converted into *fenchene*, $C_{10}H_{16}$, by boiling with aniline (page 267).

When either dextro- or lævo-fenchone in alcoholic solution is treated with hydroxylamine, it forms an *oxime*, which yields a crystalline *hydrochloride* melting at 118° to 119°. *Fenchone-oxime anhydride*, or fencholene nitrile, $C_{10}H_{15}N$, is obtained as an oil boiling at 217° to 219° when the oxime is warmed with dilute sulphuric acid. By prolonged boiling with alcoholic potash, this is converted into *fenchone iso-oxime*, or by still longer

[1] The rotatory power of thujone is variously stated, probably owing to the existence of several isomers.

treatment into *fencholinic acid*, $C_{10}H_{16}O_2$, a body parallel with campholinic acid.[1]

PULEGONE. $C_{10}H_{16}O$ (See page 252.)

This ketone was isolated by the repeated fractionation, under reduced pressure, of the portion of the oil of pennyroyal (*Mentha pulegium*) distilling under ordinary pressure between 212° and 216°. It may be purified by conversion into the bisulphite-compound.

Pulegone is colourless when freshly prepared, but soon turns yellow on exposure to air. It has an odour like that of peppermint.

On treatment with reducing agents, pulegone is converted into the corresponding alcohol, *pulegol*, $C_{10}H_{17}.OH$ (see below), which is a viscous liquid of terpineol-like odour.

ISOMERS OF PULEGONE.—When citronellol is heated for twelve hours with acetic anhydride, it is converted into the alcoholic body *iso-pulegol*, $C_{10}H_{18}O$, having an odour like that of menthol. When this compound is oxidised, it is converted into *iso-pulegone* (probably a mixture of two stereo-isomers), which differs from pulegone in not forming a crystalline bisulphite compound, and in not yielding menthol when treated with sodium. When agitated with caustic baryta, iso-pulegone is entirely converted into pulegone, having all the characters of the natural ketone.

Pulegone is reduced by aluminium amalgam to high boiling substances, while iso-pulegone is unaltered. This serves as a method for the separation of the isomers.

Wallach has described another isomer of pulegone, named by him *pseudo-pulegone*.[2]

For the detection of pulegone in iso-pulegone, equal volumes of the ketone and petroleum-ether are mixed with a little amyl-nitrite, the mixture cooled thoroughly, and a drop of hydro-

[1] For comparisons of the derivatives of fenchone and camphor see Wallach and Hartmann (*Annalen*, cclix, 324) and Schimmel & Co.'s *Report* (April, 1900, p. 56).

[2] The following table, showing the properties of the different isomeric pulegols and pulegones, is due to E. J. Parry:—

		SPECIFIC GRAVITY.	ROTATION. $[a]_D$	BOILING-POINT, °C.
$C_{10}H_{18}O$	Pulegol, ...	0.912 at 20°	. . .	103 at 15 mm.; 215 at 760 mm.
	Isopulegol, . .	0.916 at 18°	—2.7°	91 at 12 mm.
$C_{10}H_{18}O$	Pulegone, . . .	0.936 at 15.5°	+22.9°	99 at 12 mm.; 221 at 760 mm.
	Isopulegone, .	0.921 at 18°	+10.25°	85 to 90 at 13 mm.
	Pseudo - pulegone, ...	0.918 at 20°	. . .	94 at 14 mm.; 215 at 760 mm.

chloric acid added. If pulegone be present, white nitroso-pulegone separates and the liquid becomes blue in colour. One per cent. of pulegone may thus be detected.

THUJONE. TANACETONE. $C_{10}H_{16}O$ (See page 252.)

Thujone is a ketone present in the oils of thuja, tansy, and wormwood, and is apparently identical with the *salvone* or *salviol* of oil of sage.[1]

Thujone forms a tribromo-derivative, $C_{10}H_{13}Br_3O$, melting at 121°, and a carbazone melting at 171°. By treatment in alcoholic solution with sodium, it is almost entirely converted into *thujyl alcohol*, $C_{10}H_{17}.OH$, an isomer of linalol occurring in oil of tansy.

Prolonged heating with strong sulphuric acid converts thujone into *isothujone*; and when heated alone to 280°, thujone is converted into another isomer called *carvotanacetone* (see pages 381, 385).[2]

Carvone and its Allies.

Certain essential oils, of which oil of caraway is the type, contain a dihydrocymene-derivative sometimes called *carvol*, which is a substance isomeric with thymol and several other bodies. Carvol is a compound of ketonic character and is more appropriately called *carvone*. It is closely allied to limonene (identical with the so-called *carvene* of caraway oil, &c.), and carvacrol, as is shown by the table on the next page.

CARVONE (CARVOL). $C_{10}H_{14}O$

Two physical isomerides of carvone exist, having opposite and approximately equal optical activities. *Dextro-carvone*

[1] Thujone may be conveniently prepared by treating 200 grammes of wormwood oil with 200 cc. of a saturated solution of sodium bisulphite, 75 cc. of water, and 300 of alcohol. The mixture is shaken at intervals for a fortnight, when the crystals of the bisulphite-compound which separate are washed with ether-alcohol, and the thujone set free by caustic soda solution.

[2] Wallach gives the following physical constants for thujone and its isomers:—

	THUJONE.	ISOTHUJONE.	CARVOTANACETONE.
Boiling-point, °C.,	200 to 203	231 to 232	228
Specific gravity,	0.9175	0.9285	0.9373
Index of Refraction,	1.45109	1.48217	1.48350

CARVONE AND ITS ALLIES.

SUBSTANCE.	CONSTITUTION.	EMPIRICAL FORMULA.	CONSTITUTIONAL FORMULA.	SPECIFIC GRAVITY.	BOILING-POINT, °C.	SPECIFIC ROTATION, $[\alpha]_D$.
Carvene or Limonene, ...	Hydrocarbon.	$C_{10}H_{16}$	$Me.CH\left\{\begin{matrix}.CH:CH.\\ .CH_2.CH:\end{matrix}\right\}C.CHMe_2$	0.846	175	. . .
Carvacrol, ...	Alcohol.	$C_{10}H_{14}O$	$Me\ .\ C\left\{\begin{matrix}.CH:CH.\\ :C(OH).CH:\end{matrix}\right\}C.CHMe_2$	0.981	. . .	. . .
Carvenone (carveol),	Ketone.	$C_{10}H_{16}O$	$Me.CH\left\{\begin{matrix}.CH_2.CH_2.\\ .CO.CH:\end{matrix}\right\}C.CHMe_2$	. . .	218 to 220	. . .
Carvone (carvol), . .	Ketone.	$C_{10}H_{14}O$	$Me\ .\ C\left\{\begin{matrix}.CH:CH\\ .CO.CH_2\end{matrix}\right\}C.CHMe_2$	0.960	223 to 224	±62°[1]
Carvoxime, ...	Oxime.	$C_{10}H_{15}NO$	$Me.CH\left\{\begin{matrix}.CH:CH.\\ .C(NOH).CH:\end{matrix}\right\}C.CHMe_2$	. . .	71 to 72	±39°.5
Carone, ...	Ketone.	$C_{10}H_{16}O$	$CH\left\{\begin{matrix}.CH.CH_2:\\ -CH_2-\\ .CO.CH_2.\end{matrix}\right\}C.CHMe_2$	0.957	210	+173°.8; —169°.5.

[1] The *specific rotation* usually ascribed to carvone is that given in the text, but E. J. Parry (*Chemistry of Essential Oils, &c.*) states that the purest sample examined by him, from oil of caraway, had a specific rotation of +58.6°, with a density of 0.9619.

occurs to the extent of 50 per cent. in oil of caraway, together with nearly as much limonene (carvene).[1] It is also present (30 per cent.) in the oils of dill and fennel, while *lævo-carvone* occurs in the oil of *Mentha crispa*.

Pure dextro-carvone may be prepared by treating the fraction of caraway oil distilling above 190° C. with an equal measure of alcoholic ammonium sulphide, when a body of the composition $C_{10}H_{14}(OH).(SH)$ separates in long needles, which on

[1] For the separation of carvone from limonene, H. Labbé (*Bull. Soc. Chim.*, 1900, xxiii, 280) boils together 5 grammes of the oil and 15 of sodium bisulphite, with water and some sodium bicarbonate, for one and a half hours in a small flask fitted with a reflux-condenser. The product is shaken out with ether, the separated ethereal layer dried by anhydrous sodium sulphate, and the residual limonene, &c., weighed. The carvone is determined by difference.

treatment with alcoholic potash are decomposed with separation of carvone.

When boiled with excess of sodium bisulphite, carvone is converted into a body which, according to Labbé, has the formula $C_{10}H_{14}O(SO_3NaH)_2$.

On treating carvone with metaphosphoric acid, great heat is evolved and actual explosion is apt to occur. With crude caraway oil the action is less intense. In either case, the ketonic body carvone is converted into the isomeric substance *carvacrol.*

Carvone is official in the German Pharmacopœia (carvol), in which it is described as a pale yellowish or colourless liquid, having a strong odour of caraway. The specific gravity is given as 0.960 and the boiling-point as 224° C. One cc. of carvone diluted with an equal measure of alcohol is stated to remain unchanged or to assume only a slight or violet colour on addition of a drop of a very dilute solution of ferric chloride.

Carvone has the practical advantage of being much more readily soluble in dilute alcohol than is the case with oil of caraway, while it possesses all the valuable properties of the natural oil.

Determination of Carvone.

The determination of this important constituent of certain essential oils (*e.g.*, the oils of caraway, cumin, dill, spearmint, &c.) cannot be made with any degree of accuracy. Several methods have been proposed, as, for example, those based on a determination of the iodine-absorption of the oil, and on the results obtained by fractional distillation. Neither of these processes, however, gives a reliable indication of the carvone-content. The specific gravity and the optical rotation of the carvone-containing oils are, of course, valuable data, but give only a rough approximation to the percentage of carvone.[1]

[1] Assuming that caraway oil contains only limonene and carvone, and that a represents the specific gravity of the sample, the percentage of carvone (x) may be deduced from the following formula:—

$$x = \frac{(a - 0.850)100}{0.112}$$

0.850 is the specific gravity of limonene, and 0.112 the difference between this and the specific gravity of carvone (0.962).

A process in which the crystalline hydrogen sulphide addition-product is isolated and the carvone regenerated and weighed, is rendered useless as a quantitative method by the fact that the carvone hydrosulphide remains partly in solution, and also other constituents in the oils are apparently acted on by hydrogen sulphide.

Another method which has been largely employed for the determination of carvone is that in which the crystalline carvone-phenyl-hydrazone, resulting from the reaction of the carvone with phenyl-hydrazine at 100° C., is isolated and weighed after purification. The compound, however, is unstable and cannot be dried without decomposition, and the method thus gives only approximate results.

A promising method for the determination of carvone, based on the formation of a crystalline carvoxime, has been proposed and studied by E. Kremers (*J. S. C. I.*, 1901, xx, 16) and his collaborators (*J. C. S.*, 1898, ii, 358; 1900, ii, 117, 631). A known weight of the oil under examination, containing about 5 grammes of carvone, is dissolved in 25 cc. of alcohol, and 5 grammes of hydroxylamine hydrochloride and 6.5 grammes of sodium bicarbonate are added.[1] The mixture is boiled for fifteen to twenty minutes on the water-bath under a reflux-condenser; 25 c.c. of water are next introduced, and the alcohol is distilled off, a large quantity of limonene simultaneously passing over. Steam is then passed slowly through the flask and the distillation continued, collecting the last portions of the distillate in separate test-tubes till traces of carvoxime crystals appear on the surface of the liquid.[2] The distillation is stopped, the condenser rinsed with a little hot water, which, together with the last distillates, is returned to the flask. The whole is cooled, and when the oxime has solidified it is collected on a filter (removing what adheres to the flask by means of a loop of stiff wire), washed, and dried by suction. The air-dried product is finally heated for one hour on the water-bath and weighed. To the weight thus obtained 0.100 gramme is added to compensate for the loss by volatilisation and the carvoxime so corrected is calculated into carvone by the factor 0.9088.[3] The method gives results which are fairly uniform, but are usually about 2 per cent. too low. It is necessary that the directions should be strictly followed to obtain satisfactory results. Kremers considers the method by no means perfect, but of much value, and it has the advantage of yielding a definite crystalline compound.

When an oil is badly resinified, the carvoxime may refuse to crystallise, and in such case the oil should be distilled with steam, and the process carried out on the distillate. A small quantity

[1] It is desirable not to use more sodium bicarbonate than is necessary to liberate the whole of the hydroxylamine. Kremers' experiments, indeed, show that the amount of sodium bicarbonate may be advantageously reduced to 5.5 grammes instead of employing 6.5 grammes as recommended in the text. A large excess of hydroxylamine hydrochloride should be avoided. If more than 50 per cent. of carvone is supposed to be present, the amount of hydroxylamine is correspondingly increased.

[2] If the distillation of the carvoxime and alcohol mixture is not carried out carefully in the manner described, loss may be entailed by carrying the distillation too far. Schimmel & Co. failed to obtain satisfactory results by this method (*Semi-Annual Report*, October, 1896, p. 49), probably for this reason.

[3] The volatility of carvoxime in presence of water-vapour is somewhat irregular, and the drying of the compound should always be conducted under similar conditions.

of resin will increase the weight of oxime recovered, and so tend to make the results too high. The melting-point of the carvoxime, which should lie between 71° and 73° C., is lowered by the presence of resin, but no idea of the amount of impurity can be obtained in this way, as the point at which melting begins in the impure oxime is not sharp.

J. Walther (*Jour. Pharm. Chim.*, 1901, xiii, p. 32; abst. *J. S. C. I.* 1901, page 289) has proposed to determine carvone by titrating the excess of hydroxylamine hydrochloride remaining after the removal of the carvoxime.

CARVACROL. $C_{10}H_{14}O$

This body has the constitution of a methyl-isopropyl-phenol. It is isomeric with thymol, both bodies being derivatives of paracymene (pages 255, 354).

Carvacrol occurs in several essential oils, especially those of the thyme family. It is the principal constituent (50 to 80 per cent.) of Spanish oil of hops or Cretan oil of marjoram (from *Origanum hirsutum* and *Creticum*), and also occurs abundantly in the oils of caraway and pepper-wort (*Satureja hortensis*). In smaller quantity, carvacrol exists, together with thymol and cymene, in the oil from *Thymus serpyllum*.

The carvacrol occurring naturally in essential oils is probably a product of the molecular transformation of previously existing carvone, the —CH.CO—group being rearranged to form the —C:C(OH)—group. The same change can be effected by heating carvone with alcoholic potash.[1]

Carvacrol is a thick, oily liquid of peculiar aromatic odour. On cooling in a freezing mixture, it forms crystals which melt at about 1° C.

The alcoholic solution of carvacrol is not coloured green by ferric chloride until after addition of water (distinction from carvone). With phosphoric anhydride, carvacrol yields propylene and *para*-cresol.

Carveol or *Carvyl Alcohol*, $C_{10}H_{15}.OH$, is formed by the action of sodium on carvone in alcoholic solution. It is a viscous liquid, with an odour distinct from that of carvone.

Carvoxime, $C_{10}H_{14}(N.OH)$, is obtained by the action of hydroxylamine on carvone, or by heating limonene nitrosochloride with alcoholic potash. It crystallises from alcohol in transparent tables. By treatment with benzoyl chloride it

[1] Carvacrol is also produced by converting pinene into its nitroso-derivative, and acting on this with hydrochloric acid. It may likewise be prepared by fusing sodium cymene-sulphonate with three times its weight of caustic potash.

yields a compound containing $C_{10}H_{14}(NO.CO.C_6H_5)$, which crystallises from hot petroleum-spirit in lustrous needles which melt at 95°. The carvoxime from lævo-limonene is identical with that prepared from carvol. It is dextro-rotatory, while the carvoxime from dextro-limonene is lævo-rotatory to about the same extent.[1]

The characterisation of the bodies of the carvone group by means of their oximes is very unsatisfactory, as these derivatives resemble each other in melting-point and other respects very closely. In some cases, crystalline bromides can be obtained by dissolving the substance in an acetic acid solution of hydrobromic acid and adding bromine.

Semicarbazide (page 233) may be employed with advantage for the differentiation of carvone and its allies, since the compounds obtained are crystalline, whereas the corresponding oximes and hydrazones are mostly oils.[2]

In cases where semicarbazide does not give good results, amido-guanidine may be employed, the product being isolated as the picrate.

[1] By mixing lævo- and dextro-carvoximes in equal proportions they react to form the isomeric *iso-nitroso-dipentene*, which is inactive and melts at 93°. Dextro-carvoxime and isonitroso-dipentene have identical molecular weights as determined by Raoult's method.

[2] The following table by A. Baeyer (*Ber.*, xxvii, 1915) gives the melting-points and crystalline forms of the *semicarbazide compounds* of the members of the carvone group:—

Substance.	Semicarbazone.	
	Melting-point, °C.	Crystalline Form.
Thujone,	171 to 172	Acute prisms.
Carone,	167 to 169	Long needles and prisms.
Carveol,	202 to 205	Spindles or six-sided plates.
Carvotanacetone,	177 to 179	Rhombic tablets and oblique prisms.
Carvone,	162 to 163	Six-sided plates.
Dihydrocarvone,	187 to 188	Slender prisms with blunt ends.
Eucarvone,	183 to 185	Concentric aggregates of prisms.
Dihydro-eucarvone,	189 to 191	Thin plates.

The semicarbazide compounds of the ketones are very readily resolved into their components by the action of dilute acids.

SULPHURETTED BODIES IN ESSENTIAL OILS.

A certain number of essential oils contain sulphuretted bodies, usually in the form of sulphides or thiocarbimides. The most important of these oils are those of black and white mustard-seeds, garlic, and spoonwort or scurvy-grass. The following table shows the botanical origin and principal constituents of the chief sulphuretted oils:—

OIL.	BOTANICAL ORIGIN.	PRINCIPAL CONSTITUENTS.
Allium,	Entire fresh plant of *Allium ursinum.*	Vinyl sulphide;[1] vinyl polysulphides; traces of a mercaptan and an aldehyde.
Asafœtida,	Gum resin, *Ferula species.*	Compounds of the composition $C_7H_{14}S_2$; $C_{10}H_{20}S_2$; $C_8H_{16}S_2$; $C_{10}H_{18}S_2$; pinene; a sesquiterpene; and a body of the formula $(C_{10}H_{16}O)_n$ (page 214).
Garden Cress,	Flowering herb, *Lepidium sativum.*	Benzyl isothiocyanate; benzyl cyanide.
Garlic (and many oils of the *Cruciferæ.*)	Entire green plant, *Allium sativum.*	Allyl-propyl disulphide, $C_6H_{12}S_2$; di-allyl disulphide, $C_6H_{10}S_2$; compounds containing $C_6H_{10}S_3$ and $C_6H_{14}S_4$. Allyl sulphide and *terpenes are not present.*[2]
Hedge-garlic,	Root of *Alliaria officinalis.*	Chiefly allyl thiocarbimide.
Horse-radish,	Root of *Cochlearia armoracia.*	Allyl thiocarbimide.
Mignonette,[3]	Root (and leaves and stalks) of *Reseda odorata.*	Phenyl-ethyl thiocarbimide.
Mustard-seed (Black),[3]	*Brassica nigra, juncea,* &c.	Allyl thiocarbimide; cyanallyl; carbon disulphide.
Mustard-seed (White),[3]	*Brassica alba.*	Acrinyl thiocarbimide; carbon disulphide.
Onion,	Fresh herb and bulb, *Allium cepa.*	Allyl-propyl disulphide; allyl sulphide and terpenes are not present.[2]
Peppermint, American,	Dried herb, *Mentha piperita.*	Dimethyl sulphide. (See page 447.)
Spoonwort (scurvy-grass),	Flowering plant, *Cochlearia officinalis.*	Secondary butyl thiocarbimide.[4]
Thlaspi Arvense,	Herb or seed, *Thlaspi Arvense.*	Allyl thiocarbimide.

[1] VINYL SULPHIDE, $(CH:CH_2)_2S$, is a liquid of characteristic odour boiling at 101°, and has a specific gravity of 0.9125. It may be obtained from fresh allium oil by fractional distillation, after a previous treatment with sodium, by which vinyl sulphide is unattacked at ordinary temperatures. Vinyl sulphide combines with six atoms of bromine to form the compound $(C_2H_3Br_2)_2.S.Br_2$. Silver oxide converts vinyl sulphide into *vinyl oxide,* $(C_2H_3)_2O$.

[2] It is doubtful whether allyl sulphide occurs in nature. The oils of garlic, onions, *Thlaspi Arvense,* &c., were stated when first examined to consist largely of allyl sulphide, but F. W. Semmler's researches (*Arch. der Pharm.,* ccxxx, p. 434) have shown that this constituent is not present. F. Davis has, however, stated (1892) that allyl oxide and sulphide are present in the oil obtained by the steam-distillation of sliced tomatoes.

[3] The chemistry of the mustard oils is described in Vol. III, Part iii.

[4] BUTYL ISO-THIOCYANATE, or secondary butyl thiocarbimide, C_4H_9-

SPECIAL CHARACTERS OF INDIVIDUAL OILS.[1]

In the following section a few of the most important of the essential oils are described, and the methods for their examination, chiefly with a view to the detection of adulteration, fully detailed. The physical characters of those oils not described in this section will be found included in the large table at the end of the volume (p. 502).

Andropogon or Indian Grass Oils.

The oils of citronella, lemon-grass, palmarosa, ginger-grass, and vetivert or cus-cus, are all derived from tropical grasses of the genus *Andropogon*, but there is some doubt as to the particular species from which certain of the individual oils are obtained.

From the table[2] on the following page it is apparent that the andropogon oils present great variety in their physical characters and chemical composition.

Citronella Oil. (See pages 327 & 332.)

The botanical origin and general characters of this oil will be found described in the table on the next page. By far the larger portion of the citronella oil of commerce is produced in Ceylon, and is obtained by distilling the dry grass (*Lana Batu* or *Maha Pangiri*) with steam. The oil is of a pale yellow to yellowish-brown colour, and sometimes greenish owing to the presence of traces of copper. The strong odour of the oil is pleasant and melissa-like (citronellal).

According to Gildemeister and Hoffmann (The Volatile Oils), while the greater part of the citronella oil of commerce is the oil distilled from *Lana Batu* grass, a smaller portion, and that the finer and more valued oil, is derived from the Singapore

$(CH_3)CH.N:C.S$, is a pungent liquid with a disagreeable odour. It boils at 159° to 160° C., and has a specific gravity of 0.944 at 12°. Butyl isothiocyanate may be prepared artificially by heating secondary butyl iodide, $(CH_3).C_2H_5.CHI$, with ammonia, and converting the resulting monobutylamine into the mustard oil by treatment with mercuric chloride and carbon disulphide.

[1] The Editor is indebted to Mr. E. J. Parry for perusal and criticism of this section.

[2] The table is compiled from the description of the andropogon oils given by E. J. Parry in his work on *The Chemistry of Essential Oils, &c.*, which should be consulted for further details, and much general information respecting them.

CHARACTERS OF GRASS OILS.

Oil.	Botanical Origin.	Chief Country of Origin.	Specific Gravity.	Opt. Rotation.° (100 mm. Tube).	Odour.	Chief Constituents.
[1]Citronella. Indian grass	*A. Nardus.*	South Ceylon.	.885 to .920	—0° to —20°	Melissa-like.	Citronellal (10 to 20 per cent.); geraniol (50 to 70 per cent.).
Lemon-grass. Indian Verbena. E. Indian melissa	*A. Citratus.*	Cochin China, Singapore, Ceylon, Malabar, W. Indies.	.878 to .905	+3° to —3°	Verbena.	Citral, 75 to 85 per cent.
Palmarosa. Indian or Turkish Geranium	*A. Schœnanthus.*	India.	.885 to .896	+2° to —2°	Geranium.	Geraniol.
Ginger-grass	*A. Schœnanthus* (?)	India.	0.897	—2°	Geranium.	Geraniol.
Vetivert. Cus-cus (Indian Dog-grass)	Root of *A. Muricatus* (*Squarrosus.* Linn.).	India, Réunion, *Mauritius, W. I.*	1.02 to 1.03	+25° to +40°	(Characteristic.)	Contains alcohols and esters.
Camel-grass	*A. Lanigerum.*	*Himalayas, Thibet*	.915 to .919	+34° to —4°	Elemi.	Phellandrene.
. . .	*A. Odoratus.*	India.	.945 to .950	—22° to —23°	. . .	. . .

[1] Citronella oil must not be confounded with the oil distilled from the fruit of *Tetranthera citrata*, sometimes called "Javanese verbena oil."

and Java grass, *Maha Pangiri*. The following table gives the chief characters and composition of the two oils:—

	Lana Batu Oil.	Maha Pangiri and Java Oil.
Specific gravity at 15° C.	0.900 to 0.920	0.886 to 0.900
Optical rotation (100 mm.)	—5° to —21°	—0.4 to —3.0
Acetylisable constituents, per cent.	50 *to* 70	80 *to* 90
Citronellal, per cent.	28	53
Geraniol, per cent.	33	35
Methyl-eugenol, per cent.	8	0.8

Javanese oil is further stated to contain dextro-citronellol. The high specific gravity of the Ceylonese oil is due to the greater proportion of methyl-eugenol which it contains.

The solubility of both these citronella oils is the same, a clear or only faintly opalescent solution being formed on shaking with 1 to 3 volumes of 80 per cent. alcohol. When this clear solution is diluted to 10 volumes with 80 per cent. alcohol, no oily drops should separate on standing, though a mere turbidity may be disregarded if previously present.[1] This is known as "Schimmel's test" (see footnote below and on page 390).

Umney and Swinton have published results showing that the variable composition of commercial citronella oils is probably at least in part due to the fact that some distillates are produced by the aid of steam and others by the open-fire method (*Year Book Pharm.*, 1897, p. 365).

Citronella oil contains, as its chief odourous constituents, citronellal and geraniol. The terpenes camphene and dipentene, and probably limonene, constitute about 10 to 15 per cent. of the oil. Methyl-eugenol, lævo-borneol (1 to 2 per cent.), methyl-heptenone, linalol, and acetic and valeric esters, two sesquiterpenes, and possibly terpineol also occur in citronella oil.

The methods for the determination of citronellal and geraniol are fully described on page 332 *et seq.* The acetylation process when applied to citronella oil does not express the true proportion of geraniol, as is now generally recognised (p. 335). But it does give a *relative* figure, and the acetylisable constituents should always be determined.

Citronella oil has an enormous use as a perfume for cheap

[1] In order to avoid any uncertainty as to the indications given by Schimmel's test, E. J. Parry (*Chem. and Druggist*, 1901, p. 142) has proposed the use of a slightly stronger alcohol in the case of those oils which give a turbidity with 80 per cent. alcohol. Some pure oils (generally those of high specific gravity) give a clear solution with 3 or 4 vols. of 80 per cent. spirit, and subsequently a turbid solution on diluting to 10 volumes. In nearly all such cases the use of alcohol of 81 to 83 per cent. strength results in a clear solution with 10 vols. of the alcohol. If small quantities of petroleum are present, however, there is little change in the turbid solution even if 85 per cent. spirit be employed.

toilet soaps, and in consequence of the demand is very frequently grossly adulterated. Petroleum (kerosene) is much employed for such purposes, while the fixed oils are sometimes added. Either type of adulterant disturbs the ready solubility of the oil in 80 per cent. alcohol, the presence of petroleum producing a milk-white mixture and finally after long standing oily drops on the surface of the solution, while the fixed oils cause a turbid liquid, and eventually oily drops fall to the bottom of the containing vessel. Another difference in the effect of these adulterants is found in the fact that while a citronella oil containing fixed oil is not soluble in 80 per cent. alcohol in any proportion (1 to 10 volumes), oils containing an admixture of petroleum are soluble in 2 volumes of the spirit, but with 10 volumes the milk-white turbidity is produced.

Parry and Bennett have recorded the presence of 20 per cent. of alcohol in citronella oil. The oils containing this addition also contained other adulterants, the spirit being present to ensure their passing Schimmel's test. Gurjun-balsam oil has been found in adulterated oil of citronella.

One of the more recently discovered of the adulterants of citronella oil is the *light resin spirit* found by Parry and Bennett to be present to the extent of 12 per cent. and upwards in certain oils (*Chem. and Druggist,* 1903, pp. 88, 408). Although the exact nature of this adulterant is perhaps somewhat doubtful, Parry and Bennett believe it to be either pure light resin spirit or a mixture of this substance with light petroleum spirit. On fractional distillation at reduced pressure (20 mm.), such adulterated oils gave a fraction (first 10 per cent.) having a spec. gravity of 0.822, an optical rotation of —26.8°, a refractive index of 1.4490, and boiling at 150° to 160° C. at the ordinary pressure. Under similar conditions, Parry and Bennett found normal citronella oils to give a fraction having a minimum specific gravity of 0.858; optical rotation, —45° (but this is very variable); refractive index, near 1.4600, and not below 1.4570 at 20° C. The solubility of the fraction in 10 volumes of 80 per cent. alcohol should also be noted. While pure oils always yield a perfectly soluble fraction, oils containing notable proportions of resin spirit yield an insoluble fraction. The observation of these characters, and of the reduced rotation of the first 10 per cent. distilled, are stated by Parry and Bennett to suffice for the detection of the adulterant.

The following standards have therefore been suggested by Parry and Bennett for citronella oil[1] (*Chem. and Druggist,* 1903,

[1] For some time Schimmel's test (p. 389) was regarded as sufficient to detect all likely adulterants, but the discovery of light petroleum and resin spirits in citronella oils was shown by Parry and Bennett to place the test in a less satisfactory position. Thus while some of these adulter-

June 20). The limits of specific gravity and optical rotation apply only to normal Ceylon oils, and not to East Indian distillates:—

Spec. gravity at 15.5° C.,	0.900 to 0.915
Optical rotation (100 mm.),	0° to —15°
Sp. gravity of first 10 per cent. distilled (at 20 to 40 mm. pressure),	Above 0.858
Refractive index of first 10 per cent. (at 20° C.),	Above 1.4570
Solubility of oil in 80 per cent. alcohol,	To pass Schimmel's test (p. 389).
Geraniol and citronellal (acetylation method, as total geraniol),	Above 58 per cent.

Lemon-grass Oil. (See pages 327 to 343.)

This oil is obtained by distilling the fresh grass, *Andropogon citratus*, the yield being from 0.24 to 0.4 per cent. (See table on page 388 for further particulars and general characters of the oil.)

Lemon-grass oil is a yellow to brownish-red coloured oil, with a strong verbena or lemon-like odour. The majority of Ceylon and Cochin China oils have a specific gravity between 0.895 and 0.905, and an optical rotation (100 mm.) lying between the limits of +3 to —3°. Ceylon and Cochin China oils, when freshly rectified, dissolve to a clear solution in 2 to 3 parts and more of 70 per cent. alcohol, but are slightly less soluble after three months. Certain lemon-grass oils having characters outside all these limits are met with. Thus West Indian lemon-grass oil is an oil of fine odour, of specific gravity from 0.877 to 0.885, and containing 75 to 80 per cent. of aldehyde. Cameroon oils have a specific gravity about 0.885 and may contain 78 per cent. of citral.

Lemon-grass oil thus consists very largely of citral, which occurs up to a proportion of 85 per cent. In addition, methylheptenone, geraniol (partly as esters), and possibly linalol, dipentene and limonene (10 per cent. of terpenes), are present, together with small amounts of citronellal and traces of cymene,

ated oils give distinct in soluble matter with Schimmel's test, others have been found to contain 20 per cent. of the resin-spirit and yet to answer Schimmel's test. For this reason Schimmel & Co. have now described the following modified test (the so-called "Raised Schimmel's test"): Two tests are made side by side: one exactly as usual in the ordinary Schimmel's test; the other after the addition of 5 per cent. of Russian petroleum to the oil under examination. Both the original oil and that to which petroleum has been added should be soluble in 80 per cent. alcohol as employed in the test, and oily drops should not separate in either case.

normal decyl aldehyde, and possibly of another aldehyde isomeric with citral.

The *determination of citral* in lemon-grass oil is described at length on page 338 *et seq.* The bisulphite method is useful only as giving comparative results between various samples, the figures not being absolutely accurate. The presence of methyl-heptenone does not interfere with the determination of citral by the bisulphite method, since the compound formed with this ketone is decomposed at 100° C. and the free ketone is measured with the unabsorbed portion of the oil.

Lemon-grass oil should contain not less than 70 per cent. of citral. Many oils contain a much larger proportion of aldehyde but some commercial samples have suffered partial extraction of this valuable constituent.

Lemon-grass oil is frequently adulterated, and some of the additions made to the oil to increase its apparent value (as, for instance, *acetone*, found by E. J. Parry) are distinctly ingenious. Fatty oils are often added to lemon-grass oil, and occasionally petroleum. Either of these additions causes the oil to have a decreased solubility in 70 per cent. alcohol, while the specific gravity is generally disturbed.

Citronella oil was found by E. J. Parry in certain consignments of lemon-grass oil. The solution of the oil in 70 per cent. alcohol quickly became cloudy on cooling, pure oils requiring somewhat prolonged cooling of this solution to produce cloudiness. Citronellal was readily detected in the bisulphite compound separated from the oil.

Acetone has also been found by Parry in certain lemon-grass oils of slightly low specific gravity (0.893). The apparent percentage of citral was 76. Distillation of such oils at the ordinary pressure gave about 11 per cent. of distillate (chiefly acetone) below 60° C.

Lemon-grass oil is largely used in perfumery, and has been employed in the adulteration of lemon oil. An important use to which lemon-grass oil is now put is in the manufacture of *ionone*, the artificial violet perfume produced from lemon-grass citral.[1]

[1] Ionone is prepared commercially from lemon-grass citral by Tiemann's process of condensation with acetone in the presence of alkalies, or by means of ethyl aceto-acetate or similarly acting substance. The product of the reaction, pseudo-ionone, $C_{13}H_{20}O$, is converted into the isomeric ketone "ionone" by heating with dilute sulphuric acid and glycerin (or acid alone) or by the use of alkalies in a similar manner. Ionone possesses (when diluted by solution in alcohol) a characteristic odour resembling that of violets and is much used as a perfume.

Commercial "ionone" as thus prepared has been shown by Tiemann to be a mixture of two stereo-isomers, now named α-ionone and β-ionone, of which the latter is the more desirable as a violet perfume. Ionone is

Palmarosa Oil. INDIAN GERANIUM OIL. (See page 327.)

This oil, sometimes misnamed Turkish geranium oil, is the product of the grass *Andropogon Schœnanthus*, which yields about 0.3 per cent. of a pale yellow to darker coloured oil (according to the method of distillation). The oil has a characteristic geranium or rose-like odour, and contains a large proportion of geraniol, chiefly free, though from 5 to 15 per cent. of esters (geranyl acetate and caproate) are generally present. In addition, the oil contains a small quantity of dipentene, and possibly of methyl-heptenone. The free geraniol present varies from 65 to 85 per cent. in pure oils, as determined by acetylation, while the total geraniol should not be less than 75 per cent. and frequently reaches a much higher figure (to 93 per cent.). The esters present absorb from 3 to 5 per cent. of KOH.

Palmarosa oil should dissolve to a clear solution in 3 volumes of 70 per cent. alcohol. Many adulterants interfere with the solubility of the oil, such as the oils of gurjun balsam and turpentine, and petroleum, fixed oils (especially cocoanut oil) and cedar-wood oil. Fixed oils leave a non-volatile residue, and the ester value and geraniol content are lowered by such additions of oil of turpentine, which also lowers the specific gravity, as does the presence of petroleum. Oils containing an admixture of cocoanut oil frequently partially solidify in a freezing-mixture.

Palmarosa oil is not related to true geranium oil in any way, but it possesses an odour similar to the latter oil. Palmarosa oil is much employed in cheap perfumery, and finds use also as an adulterant of rose otto and of true geranium oil.

found on the market in the form of a 10 per cent. solution in alcohol. The chemistry of these synthetic ketones will be found described at some length in Parry's *Chemistry of Essential Oils, &c.*

The following table summarises the characters of these bodies:—

	COMMERCIAL "IONONE."	α-IONONE.	β-IONONE.	PSEUDO-IONONE.
Specific gravity at 15° C., ...	0.935	0.934	0.949	0.904
B. Pt. at 12 mm. pressure, ° C....	126 to 128°	123 to 124°	127 to 129°	143 to 145°
Refractive index (at 17° C.), ...	1.507	1.500	1.520	1.5335
Optical rotation,	inactive.	...	...	...
Oxime, M. Pt. ° C.	90°	89 to 90°	Liquid	...
Semi-carbazone, M. Pt. ° C., ...	*110°*	*107 to 108°*	*148 to 149°*	...

The ionones possess the constitution shown by the formula:—

$$(CH_3)_2C<\begin{matrix}CH(CH:CH.CO.CH_3).CH.CH_3 \\ CH_2.CH\text{———————————}\end{matrix}>CH$$

Methods for the recognition and separation of the ionones in violet-scented preparations have been published by R. Schmidt (abst. *J. S. C. I.*, 1900, p. 380).

Angelica Oil.

This oil is present in all parts of the herb *Angelica officinalis* (*Angelica Archangelica*), but is mainly distilled from the roots only. According to Schimmel & Co., however, the finest oil is that distilled from the fruit (seed).

Angelica-root oil, when distilled from the fresh material, is a nearly colourless or light yellow oil, having a pronounced aromatic odour and a pungent taste. By exposure to air and light, the oil becomes of a yellow or brownish colour. On long standing the oil deposits a crystalline body. Giordani found this compound to melt at 74° to 77° C., and to have the composition $C_{32}H_{62}O_5$.

The following table shows the properties of angelica oil,[1] according to the character of the plant used for distillation:—

Material Used.	Sp. Gr. of Oil at 15° C.	Optical Rotation ° (in 100 mm. Tube).	Constituents.
Fresh root,	0.857 to 0.905	+18 to +30	Methyl-ethyl-acetic acid; *d*-phellandrene; oxypentadecylic acid; two crystalline bodies.
Dried root,	Up to 0.918	....	....
Whole herb,	0.869 to 0.890	+ 8 to +25	....
Fruit (seed),	0.856 to 0.890	+10 to +13	Phellandrene; methyl-ethyl-acetic acid; oxymyristic acid.

It was shown by Beilstein and Weigand in 1882 (*Berichte*, xv, p. 1741), and by Naudin in 1883 (*Bull. Soc. Chim.* [2], xxxix, 407), that oil of angelica-root contained terpenes, of which dextro-phellandrene has since been recognised by Schimmel & Co. (*Report*, April, 1891). Pinene and cymene are probably also constituents of this oil, whilst the presence of one or more sesquiterpenes has been inferred from the high boiling-point (250°) of the heavier fractions.

Ciamician and Silber (*Berichte*, xxix, p. 1811) have isolated from angelica-root oil two crystalline bodies, which are stated to have the constitution of anhydrides of oxyacids. Angelica oil also contains methyl-ethyl-acetic acid and oxypentadecylic acid, $C_{15}H_{30}O_3$, the latter substance crystallising from ether in groups of needles, melting at 65° C. As has been pointed out by Schimmel & Co., it is worthy of note that the oxypentadecylic acid present in angelica-root oil is replaced by oxymyristic acid,

[1] Three samples of angelica-root oil examined by Haensel showed specific gravities of 0.854 to 0.856 and optical rotation, +38° to +39°. An oil from the dried root had a specific gravity of 0.875, and an optical rotation of +23.6°.

a lower homologue, in the oil from angelica-fruit. Angelica-root oil finds its chief employment in the manufacture of liqueurs.

JAPANESE ANGELICA-ROOT OIL is the product of the plants *Angelica anomala* and *A. refracta*. The specific gravity of the oil is about 0.910 at 20° C. It has an acrid odour, but resembles musk to some extent. At a temperature of 10°, crystals separate from the oil, which solidifies to a pasty mass at 0° C. These crystals melt at 62° to 63°, and have all the characters of a fatty acid, possibly oxypentadecylic acid.

The boiling-point of the oil is between 170° and 310° C., the high-boiling fractions having a bluish-green colour. The oil does not appear to have been further examined.

Anise Oils.

True anise oil is obtained from the fruit of *Pimpinella Anisum*. The oil of star-anise is obtained from the fruit of *Illicium verum*, and constitutes the bulk of the oil of anise found in commerce. Both oils are recognised in the British Pharmacopœia (1898) and in the U. S. Pharmacopœia (8th Rev.). An oil produced from *Seseli Harveyanum*, known in some parts of Australia as "anise oil," has more of the appearance and flavour of fennel oil.

Anise oil (from *Pimpinella Anisum*) contains anethol, methyl-chavicol and possibly anise-ketone,[1] with small quantities of anise-aldehyde and anisic acid. W. A. Tilden states that dextro-pinene is also present. In addition to these constituents, oil of star-anise contains dextro-pinene, lævo-phellandrene, safrol, and the ethyl-ether of hydroquinone. According to Tardy, terpineol is also present.

The physical characters of the two varieties of anise oil are practically identical. Oil of anise is a pale yellow and somewhat thick oil. The British Pharmacopœia (1898) directs that it should congeal when stirred at temperatures between +10° and +15° C., and should not become liquid again below +15°. The specific gravity at 20° should be 0.975 to 0.990. A normal oil should not melt at a temperature lower than +15° C., the usual range being about +15° to +18° or 19° C. The melting-point is determined in the following manner:—A small quantity of the oil contained in a narrow test-tube is first immersed in a freezing mixture. A trace of crystallised oil of anise may be added to accelerate crystallisation. The temperature is then

[1] Bouchardat and Tardy (*Compt. rend.*, cxxii, page 198) found a sample of Russian anise oil to contain small quantities of anise-ketone and fenchone. The sample examined by them, however, was not a normal oil, since it had a melting-point of 10° C. and was dextro-rotatory. It is most probable, therefore, that the sample in question was adulterated with fennel oil.

slowly raised, a thermometer with its bulb immersed in the oil being used as a stirrer. The oil should not become liquid below 15° C. *Care should be taken that the sample is well mixed* before using a portion for the determination of the melting-point.

It is necessary to observe the melting-point of the solidified oil, since the solidifying point is rendered useless by the fact that anise oil has a tendency to remain liquid below its true congealing point (J. C. Umney, *Pharm. Jour.*, 1889, p. 648).[1] If the solidified oil has a melting-point below 15°, the sample has either suffered admixture with some foreign oil, or a portion (or the whole) of its anethol has been removed.[2] Spermaceti is said to have been used as an adulterant of anise oil. If present in notable amount, spermaceti would lower the specific gravity and raise the melting-point. The solubility of the oil in alcohol would also be reduced. Pure anise oil should dissolve to a perfectly clear solution in three parts of 90 per cent. alcohol. Oxidised oils are more soluble, completely oxidised samples dissolving in rectified spirit in all proportions.

The presence of methyl-chavicol, the isomer of anethol, in anise oil, is shown by the action of boiling alcoholic potash on the anethol-free oil. The boiling-point of the liquid is raised, and on cooling, a further large quantity of anethol crystals is produced.

The constituents of oil of anise gradually undergo oxidation on keeping the oil, a rise in its specific gravity being produced, while the melting-point is lowered. Oxidised oils show the presence of notable quantities of anisic aldehyde when shaken with sodium bisulphite solution (25 per cent.), whereas fresh oils give no such reaction. Oils examined by this test should be kept at 20° to prevent crystallisation of anethol.

The value of oil of anise depends upon its content of anethol. The proportion of this constituent may be approximately determined by cooling the oil to a low temperature, and after crystallisation has taken place, pressing the crystals between blotting-paper, and weighing the anethol thus obtained. The amount of anethol present in anise oil may also be determined by fractionally distilling the oil, and collecting the fraction coming over between 225° and 235° C. separately (anethol boils at 232°). The measure of this fraction corresponds very nearly to the content of anethol. Good samples of anise oil generally contain

[1] The U. S. Pharmacopœia, however, directs that the *congealing* point of anise oil be observed as described, the highest temperature obtained during the solidification being noted as this point, which should not be below 15° C.

[2] According to Pancoast and Kebler (*Amer. Jour. Pharm.*, 1901, p. 356), pure anise oils having a low congealing-point are sometimes met with. They are obtained from a mixture of natural and artificially ripened seeds, and are known as "Flower Oils."

at least 85 per cent. of anethol, and the amount should not be less than 80 per cent.

The two oils of anise are slightly lævo-rotatory, usually about —1° to —3°. This figure is a valuable indication of the purity of anise oils, since their adulteration with fennel oil (or its stearoptene) causes them to show dextro-rotation.[1] This is due to the presence of fenchone, which in the case of adulteration with the stearoptene of fennel oil is retained to a sufficient extent in the stearoptene to cause the product to be more or less dextrorotatory, according to the amount of adulterant present.

Petroleum is sometimes added to anise and star-anise oils. This adulterant causes the oils to be less soluble in alcohol, and lowers the specific gravity, but the melting-point will not be greatly modified. For the determination of petroleum, the oil may be heated with concentrated sulphuric acid, when the residue consists of petroleum. J. C. Umney found from 37 to 56 per cent. of this adulterant in anise oils. The separated petroleum had a specific gravity of 0.835.

J. C. Umney (*Chem. and Druggist*, 1899, liv, 323) considers that the differences in the physical characters of star-anise oils are caused by distillation from raw materials, oils in some parts of China being produced from the leaves and twigs of the star-anise.[2] Umney found that the oil distilled from the leaves had a specific gravity of 0.9878, and an optical rotation of +1°. The oil, however, remained fluid even at +8° C. By fractional distillation, the oil was found to be rich in anise aldehyde, which usually only occurs in partially or wholly oxidised oils of anise and star-anise. It is probable that the presence of anise aldehyde in star-anise oil is the cause of the difference in odour between oil of anise and star-anise.

The two oils of anise are said to be distinguishable by the following colour test:—A saturated solution of hydrochloric acid gas, when added to the oil, gives with anise oil a deep blue coloration, and with star-anise oil, a yellow or brown coloration.

According to J. C. Umney, the so-called "Australian anise oil" has a specific gravity of 0.914, and an optical rotation of +19°. It does not become crystalline at +4° C. The oil appears to resemble fennel oil more than ordinary oil of anise.

[1] According to E. Dowzard, however, some samples of pure anise oil show slight dextro-rotation, from +0.03° to +0.7°.

[2] E. J. Parry (*Chemistry of Essential Oils, &c.*) favours the view that the differences observed in the commercial oils of anise are not due to the cause ascribed by Umney, but to the fact that the flowers or very early fruits of the plant (removed to allow the remaining fruits to mature to better advantage) are distilled, yielding an oil containing a lower percentage of anethol. Parry examined an oil of this description with the following results:—Specific gravity, 0.9916; optical rotation, +0.3°; solidifying-point, +12° C.

The physical constants and characters of other unimportant varieties of anise oil are described in the table on page 503.

Bay Oil.

This oil, which has frequently been described as being obtained from the leaves of *Myrcia acris*, is, according to E. M. Holmes (*Pharm. Jour.* [3], (1891), xxi, p. 837), the product of *Pimenta acris*. Both the fresh and the dried leaves have been employed in the distillation of this oil.

Oil of bay is not official in the British nor the U. S. Pharmacopœia, but was contained in the U. S. Pharmacopœia (1890). The specific gravity of the oil varies from 0.965 to 0.985, being usually about 0.970. E. J. Parry (*Chemistry of Essential Oils*) gives the normal specific gravity of the oil as from 0.965 to 0.995. Oils of higher specific gravity should be regarded with suspicion, being possibly adulterated with oil of pimento or cloves.

The optical rotation of bay oil should not exceed —2° in a 100 mm. tube. Adulteration with oil of turpentine will alter this figure considerably.

The composition of bay oil cannot yet be regarded as settled beyond doubt. Mittmann (*Arch. Pharm.*, ccxxvii (1889), p. 529) found it to contain pinene, dipentene, eugenol, and methyl-eugenol. In a subsequent research by Power and Kleber (*Pharm. Rundschau*, New York, 1895, xiii, p. 60), the presence of Mittmann's two terpenes was not confirmed, although lævo-phellandrene was found in the oil. Power and Kleber also recognized the following bodies as being constituents of bay oil:—eugenol, methyl-eugenol, chavicol, methyl-chavicol, citral, and "myrcene," an open-chain hydrocarbon of the formula $C_{10}H_{16}$, which distilled over between 67° and 68° C. at 20 mm. pressure, and had the specific gravity 0.8023.

Bay oil suffers adulteration with several oils, chiefly those of cloves, pimento, and turpentine. The two former may be detected by the high specific gravity of the oil, and by the following test, as was directed by the U. S. Pharmacopœia (1890):—"If to three drops of the oil contained in a small test-tube five drops of concentrated sulphuric acid be added, and after the tube has been corked, the mixture be allowed to stand for half-an-hour, a resinous mass will be obtained. On adding to this mass 4 c.c. of diluted alcohol, vigorously shaking the mixture, and gradually heating to the boiling-point, the liquid should remain nearly colourless, and should not acquire a red or purplish-red colour (distinction from oil of pimento and oil of cloves)."

Turpentine oil, when present as an adulterant, may be de-

tected in the first fraction of the distilled oil of bay by means of the nitrosochloride reaction for pinene (page 258) which, according to Power and Kleber, is not present in pure oil of bay.

When freshly distilled, oil of bay is easily soluble in 90 per cent. alcohol. On keeping, its solubility becomes slightly lessened.

The phenolic constituents of oil of bay (eugenol and chavicol) are present in considerable quantity, and a determination of their amount is a valuable aid in determining the purity of the oil. For their determination, Thoms' process, as described on page 362, is perhaps the most accurate. As shown by this method, the proportion of phenolic constituents in genuine oil of bay ranges from about 59 to 65 per cent.

Oil of bay finds its chief employment in perfumery, notably in the manufacture of Bay Rum.

CALIFORNIA BAY OIL is in every respect different from the true oil of bay. The Californian oil is obtained by the distillation of the leaves of *Laurus californica*, a tree commonly known as the mountain-laurel or Californian olive tree. The oil is a light yellow liquid, with a specific gravity of 0.930 to 0.950 (E. J. Parry, *Chemistry of Essential Oils, &c.*). According to Heaney (*Amer. Jour. Pharm.*, 1875, p. 105), the oil contains a hydrocarbon of specific gravity 0.894, and boiling-point 175° C. The oil appears to contain cineol, but little definite is known of its composition.

Bergamot Oil.

This oil is obtained by expression of the fresh peel of the ripe fruit of the ordinary bergamot, *Citrus bergamia*. It is a green coloured oil having a very pleasant odour and a bitter taste. Rectification deprives the oil of its green colour,[1] but the oil thus produced is much inferior in quality to undistilled bergamot oil, the esters being decomposed and thus considerably reduced in amount (12 to 15 per cent. or less).

The specific gravity of oil of bergamot ranges from 0.882 to 0.886, and in some seasons to 0.888. The distilled oil has a specific gravity of 0.870 to 0.880. Bergamot oil has an optical rotation of +8° to +20° for 100 mm. Many oils are too dark for the observation of the rotatory power to be made in a 100 mm. tube, so that 50 mm. or 20 mm. tubes must be employed.

Freshly expressed oil of bergamot deposits a white, odourless and tasteless substance known as *bergaptene*. Bergaptene crystal-

[1] The green colour is in all probability due to the presence of chlorophyll in the oil. Gildemeister and Hoffmann, however, state that the presence of copper causes the coloration (*The Volatile Oils*, page 473).

lises in needles having the composition $C_{12}H_8O_4$, and melting at 188°. It is the methyl-ether of a dioxycoumarin; or the inner anhydride of bergaptenic acid, $C_{11}H_8O_2.(OH).COOH$. On fusing bergaptene with caustic potash, phloroglucin is formed. According to Soden and Rojahn, bergaptin, a body melting at 59°, is also present in the oil. In addition to these solid constituents, bergamot oil contains dextro-limonene; dipentene (?); linalol; and linalyl acetate (30 to 42 per cent.). Octylene, pinene, camphene and acetic acid are also said to be present. The odour of the oil is much richer than is that of linalyl acetate alone, and thus other odoriferous constituents, as yet unknown, exist in the oil. Bergamot oil gives no reaction with Schiff's reagent, and thus, unlike orange and lemon oils, it contains no aldehydic body.

According to Charabot (*Bull. Soc. Chim.*, xxi, 1083), the linalol first produced in the fruit is largely converted into ester, during ripening, by the free acetic acid present, while a small amount of the alcohol is dehydrated, producing terpenes. Schimmel & Co. have shown that the proportion of linalyl acetate increases as the fruit ripens. The following figures illustrate this (S. & Co.'s *Semi-Annual Report*, April, 1896):—Oil from unripe fallen fruits, 25 per cent. esters; from unripe plucked fruits, 33 to 34 per cent.; from average ripe fruits, 37 per cent.; and from somewhat over-ripe fruits, 44 per cent. of esters (linalyl acetate).

Most genuine bergamot oils show an ester-content of from 35 to 42 per cent. Some pure oils occasionally contain only 30 per cent. of linalyl acetate, but this low figure should be regarded with suspicion. Within limits, the value of the oil, which is chiefly used for perfumery, depends upon the percentage of esters it contains. For this reason, it is important to bear in mind that the presence of fatty oils and resins (colophony, &c.), adulterations frequently practised, will increase the apparent content of esters.

The presence of the waxy constituents in bergamot oil (bergaptene, &c.) causes it to leave a considerable residue on evaporation at 100° C., which residue, in the case of genuine oils, ranges from 4 to 6 per cent.[1] If more than 6 per cent. of residue remain, the oil is probably adulterated, and should be examined for the presence of fatty oils and resins by determining its saponification-value. A soft, green, homogeneous residue, not exceeding 6 per cent., is obtained in the case of genuine oils. Bergamot oil, when pure, is usually soluble in half its volume of 90 per cent.,

[1] A known weight of the oil (say 2 grammes) is heated at 100° until the odour has completely disappeared. The residue is cooled and weighed. Published analyses show that this residue always contains a small amount of linalyl acetate (1 to 2 per cent.).

and in 2 volumes of 80 per cent., alcohol. The presence of fatty oils (except castor oil) interferes with this solubility.

Besides adulteration with fatty oils and resins, bergamot oil suffers adulteration from oils of turpentine, lemon and orange, and from distilled bergamot oil (obtained by rasping the peel of injured fallen fruits and distilling the product with water). Oils of turpentine, lemon, and orange decrease the gravity, solubility, fatty residue, and the proportion of esters, while lemon and orange oils raise the optical rotation. The density is increased, on the other hand, by the addition of fatty oils, cedar-wood oil, and gurjun balsam. Synthetic esters and lemon terpenes are frequently added together to bergamot oils. An addition of distilled bergamot oil lowers the ester-content and the residue non-volatile at 100° C. Fractional distillation should be carried out on all oils suspected to contaiu oil of turpentine and added terpenes.

S. Gulli (*Chem. and Druggist*, 1901, p. 383) has described a new adulterant of bergamot oil, which is prepared by treating oil of turpentine with hydrochloric acid gas to saturation (pinene hydrochloride?). This preparation can be added to bergamot oil to the extent of about 10 per cent. without materially altering the constants of the oil or interfering greatly with the ester-value (1 to 2 per cent. lower). Gulli recommends that in the case of doubtful samples, several grammes of the oil be saponified with alcoholic potash, the liquid evaporated to dryness and the residue ignited. The aqueous solution of the residue should then be tested for the presence of chlorides with silver nitrate.

NERO OF BERGAMOT is the name given to the oil obtained by expression of the peel of unripe or damaged fruit fallen from the tree. The oil is brownish-green in colour, has not a very fragrant odour, and contains only about 20 to 25 per cent. of esters. A sample examined by G. Fabris (*Analyst*, 1900, page 295) showed 25.5 per cent. of linalyl acetate, and had a specific gravity of 0.885; optical rotation at 20°, +9.5°; residue at 100°, 2.70 per cent., containing 1.75 per cent. of linalyl acetate.

OIL OF BERGAMOT LEAVES is rarely obtained pure. It is sometimes used as an adulterant of orange oils. It has a gravity of 0.870 to 0.873, an optical rotation of +25° to +26°, and is soluble in an equal volume of 90 per cent. alcohol. It contains 32 to 34 per cent. of esters (calculated as linalyl acetate), including methyl anthranilate.

The so-called *oil of wild bergamot* (from *Monarda punctata* and *M. fistulosa*) is stated by Braudel and Kremers to contain thymoquinone and hydro-thymoquinone. In addition, the oil from *M. punctata* contains cymene, thymol, and dextro-limonene; while that from *M. fistulosa* contains cymene, carvacrol, and limonene.

Cajuput Oil.

This oil is official in the British Pharmacopœia (1898) and in the U. S. Pharmacopœia (8th Rev.), and is distilled from the leaves of *Melaleuca leucadendron*. Many other species of this plant produce oils very similar to the official oil (e. g., *Melaleuca minor*, *M. uncinata*, *M. acuminata*, *M. viridiflora*, &c.).

The British Pharmacopœia describes oil of cajuput as a bluish-green oil, having an agreeable, penetrating, camphoraceous odour, and an aromatic, bitterish camphoraceous taste. It has a specific gravity of 0.922 to 0.930.[1] The oil should become semi-solid on being stirred, when cold, with one-third or one-half its volume of phosphoric acid (of specific gravity 1.75). This test ensures the presence in the oil of a due proportion of cineol.

The U. S. Pharmacopœia (8th Rev.) describes oil of cajuput as having a specific gravity of 0.915 to 0.925 at 25° C. and being soluble in one part of 80 per cent. alcohol. The oil should be lævo-rotatory (not more than —2° for 100 mm.) and should be free from *copper*. It should contain at least 55 per cent. of cineol (by volume) when assayed by the phosphoric acid process, the phosphate being decomposed by warm water and the resulting cineol measured (see page 422).

The specific gravity of cajuput oil is lowered by adulteration with turpentine oil. Oils containing less than the normal amount of cineol will also show a low specific gravity.

The bluish-green color of cajuput oil is chiefly due to the presence of traces of copper. The rectified oil is quite colourless.

Cineol (eucalyptol) is the chief constituent of cajuput oil. Terpineol, terpinyl acetate, and one or more terpenes are also present. The different varieties of oil differ in certain respects from each other in properties and in their composition. Some varieties (*M. leucadendron*, &c.) contain several fatty compounds, such as butyric and valeric aldehydes. Bertrand (*Bull. Soc. Chim.*, 1893, p. 432) found that *M. viridifolia* gave an oil (known as "Essence of Niaouli") similar in odour to oil of cajuput, and containing cineol, terpineol, valeric and benzoic aldehydes, valeric acid and terpineol valerate, dextro-pinene and lævo-limonene, methyl salicylate, and a sulphur compound.

Cajuput oil is generally slightly lævo-rotatory, ranging from

[1] Some foreign Pharmacopœias (Italian, Japanese, &c.) allow a lower limit than 0.922. The average oil of cajuput varies very little from the B. P. limits, although of recent years the specific gravity of many pure oils has slightly decreased (to 0.918) owing to a lowered cineol content. Cajuput oil oxidises on exposure to air, the small quantities of butyric, valeric, and benzoic aldehydes being converted into the corresponding acids. The slightly acid reaction of crude cajuput oil is probably due to saponification of the terpenyl acetate and to the above-mentioned oxidation of the aldehydes. Exposure of the oil to light causes polymerisation.

0° to —3°. The oil from *M. acuminata*, however, is stated to have an optical rotation of —15°.

Cineol is best determined by the process described on page 422 (footnote 1). Oils of good quality yield 60 to 65 per cent. of cineol, and about 50 to 55 per cent. should be fixed as the minimum limit for this constituent. As already stated, the U. S. Pharmacopœia requires cajuput oil to contain at least 55 per cent. by volume of cineol. Eucalyptus oil is sometimes added to cajuput oil which has been deprived of a portion of its cineol. Cajuput oil of good quality should give 60 per cent. of distillate between 175° and 185° C.

The following characters of the oils from various species of *Melaleuca* are given by E. J. Parry (*Chemistry of Essential Oils*):—

Melaleuca Species.	Spec. Gravity.	Boiling Point, °C.	Optical Rotation °. (100 mm.).
M. decussata, ...	0.938	183 to 209	....
M. ericifolia, ...	0.899 to 0.902	149 to 184	+26
M. linarifolia, ...	0.903	175 to 187	+11
M. Wilsonii, ...	0.925	....	....
M. uncinata, ...	0.925	175 to 180	+1.7
M. leucadendron (*var. lancifolia*), ..	0.955	....	—3.6
M. acuminata, ...	0.892	....	—15.3

Camphor Oil.

Camphor oil is a liquid occurring with camphor, and obtained as a secondary product in the extraction and refining of that compound (page 367). The method of manufacture as carried out in Japan has been described by H. Oishi (*Chem. News*, 1884, l, p. 275), who states that the crude camphor oil (sp. gr. 0.959) obtained by pressing the semi-solid mixture of camphor and oil (from the distillation of the wood with steam) still contains a considerable amount (20 to 30 per cent.) of solid camphor which can be recovered by fractional distillation.[1] The camphor oil thus purified is described by Oishi as a colourless liquid which gradually turns yellow by exposure to air and has a specific gravity of 0.895.

P. MacEwan, writing in 1885 (*Pharm. Jour.* [3], xv, 1045), states that Borneo camphor oil from *Dryobalanops aromatica* differs from the oils from Formosa and Japan in not undergoing

[1] On distillation, the crude camphor oil gave 6 per cent. over below 150° C., about 24 between 150° and 170°, 38 between 170° and 180°, and 19.0 per cent. between 180° and 198°, leaving a residue in the retort of 13 per cent.

any change on exposure to a low temperature. MacEwan found that if 2 c.c. of nitric acid of 1.42 specific gravity were allowed to act on a few drops of Japanese camphor oil for one minute, and the mixture was then diluted with 2 c.c. of water, the clear aqueous liquid acquired a crimson colour, whereas Formosa oil when similarly treated gave a milky solution having a scarcely perceptible green shade. MacEwan suggests the coloration produced on treating Japanese camphor oil with nitric acid as a means of detecting its presence in oil of wintergreen, said to be adulterated with it in the United States.

H. Yoshida (*J. C. S.*, 1885, p. 779) examined a sample of camphor oil five years old and gives the following as its approximate composition:—Lævo-pinene, 7 per cent.; limonene, 20; camphor, 23; and "camphorogenol" (boiling at 212°) about 50 per cent. To the last constituent Yoshida attributes the formula $C_{10}H_{18}O_2$, but C. T. Kingzett believes it to be merely a solution of camphor in camphor oil (*J. S. C. I.*, vii, 549).

The following definite compounds are stated by Schimmel & Co. to exist in camphor oil:—

CONSTITUENT.	FORMULA.	BOILING-POINT, °C.
Pinene,	$C_{10}H_{16}$	158 to 162
Phellandrene,	$C_{10}H_{16}$	170
Cineol,	$C_{10}H_{18}O$	176
Dipentene,	$C_{10}H_{16}$	180
Camphor,	$C_{10}H_{16}O$	204
Terpineol,	$C_{10}H_{18}O$	215 to 218
Safrol,	$C_{10}H_{10}O_2$	232
Carvacrol,	$C_{10}H_{14}O$	236
Eugenol,	$C_{10}H_{12}O_2$	248
Sesquiterpene,	$C_{15}H_{24}$	274

In the fractions of camphor oil of highest boiling-point there occurs a compound of an intense blue colour, which is probably identical with the body, boiling at about the same temperature, present in the oils of chamomile, millefolium, wormwood, &c. Caprylic acid is also stated by Schimmel & Co. to be present in camphor oil, and an acid, $C_9H_{16}O_2$, belonging probably to the oleic series.

Safrol is obtained on a large scale by cooling the fraction of camphor oil distilling at about 232°. The safrol crystallises out and is separated from the adherent liquid by a centrifugal machine. Much of the camphor oil which reaches Great Britain has already been deprived of its safrol.

Eight samples of commercial camphor oil purchased in Philadelphia and New York were found by Trimble and Schröter (*Amer. Jour. Pharm.*, June, 1889) to have the following characters:—

	Origin of Sample.	Specific Gravity at 15° C.	Boiling-point ° C.	Optical Rotation ° for 100 mm.	Colour.	Odour.
1.	Crude Japan Oil, ...	0.9632	180	+ 24.5	Reddish brown.	Camphor and sassafras.
2.	From Fritzsche Bros.,	0.9816	180	+ 16.3	Dark brown.	Camphor and sassafras.
3.	From Fritzsche Bros., "Germany,"	0.8877	170	+ 30.5	Colourless.	Turpentine and camphor.
4.	} Probably the same	0.8863	170	+ 31.1	Same as No. 3.	Same as No. 3.
5.	} as No. 3, ...	0.8803	...	+ 31.1	Same as No. 3	Same as No. 3.
6.	New York; "Rectified,"	1.006	210	+ 14.3	Light yellow.	Sassafras and *slightly* camphoraceous.
7.	Philadelphia, ...	0.9903	206	+ 19.2	Yellow.	Same as No. 6.
8.	Philadelphia, ...	0.9546	198	+ 0.5	Dark reddish brown.	Empyreumatic and camphoraceous.

It is clear that from some of these (*e. g.*, samples 3, 4, and 5) the safrol had been previously separated. They were, further, probably mere fractions of the residual oil, and suitable only for turpentine substitutes.

All the samples had an acid reaction, due to the presence of acetic and formic acids, and were miscible in all proportions with 95 per cent. of alcohol.

On further examination of sample No. 1, negative results were obtained with sodium bisulphite and alcoholic ammonium sulphide; alcohol and fixed oils were found to be absent, and an alcoholic solution of ferric chloride produced no coloration. When the oil was agitated with water, the acidity was removed. When the neutralised oil was boiled for some hours with aqueous caustic alkali, and the product acidulated with a mineral acid, it separated into two layers, and on subsequently distilling the aqueous portion, the distillate contained butyric, acetic, and formic acids, pointing to the presence of the corresponding esters in the original oil.

Sujiyama (abst. Schimmel's *Report*, October, 1902) found six samples of light camphor oil to range in specific gravity from 0.870 to 0.910, and to yield the following amounts of distillate on fractionation:—from 26 to 38 per cent. between 175–180°; 30 to 44 between 180–185°; 11 to 19 between 185–190°; 4 to 7 between 190–195°; 2 to 4 between 195–200°; and from 4 to 6 per cent. at temperatures exceeding 200° C.

Under the title of "*light camphor oil*," Schimmel & Co. have introduced into commerce the lower-boiling fractions of the bye-product obtained in the manufacture of safrol. It is stated to have a specific gravity of 0.895 to 0.900,[1] a flash-point of 44.5°,

[1] E. J. Parry states that samples of this oil from the London market

and a boiling-point of 175°. Rectified light camphor oil has been recommended as a substitute for oil of turpentine. Although it cannot adequately replace the latter in the manufacture of paints, light camphor oil is said to be a useful solvent for resins.

"*Heavy camphor oil*," as manufactured by Schimmel & Co., is a light green liquid boiling at 240° to 300°, and having a specific gravity of 0.960 to 0.970. It is stated to be a good solvent for all sorts of resins, including caoutchouc, and is employed for scenting soft soap, blacking, &c., and for covering the odour of mineral oil and of fats extracted by carbon disulphide or petroleum spirit. It is viscous, non-poisonous, not readily inflammable, and has marked antiseptic properties. A well-rectified camphor oil, containing much safrol and of specific gravity 1.050, constitutes the bulk of the so-called American sassafras oil on the market.

For the determination of camphor in camphor oil, H. Löhr (*Chem. Zeit.*, 1901, xxv, 292; abst. *J. S. C. I.*, 1901, p. 510) proceeds as follows:— At least 300 grammes of the oil is fractionated, the distillate below 195°, and those between 195°–220° and above 220°, being collected separately. The second fraction, which contains the whole of the camphor, is kept in a freezing mixture for one hour, when the camphor is filtered off, wrapped in filter-cloth and then in filter-paper, and pressed for half-an-hour. The cake of camphor thus obtained is wrapped in fresh filter-paper and again pressed for fifteen minutes, and is then weighed. The mother-liquor from which the camphor was previously separated is next redistilled and the fraction at 205° to 220° frozen and treated as before. Five distillations are necessary to obtain all the camphor from the original fraction containing it.

Caraway Oil.

Caraway oil is obtained by the distillation of the fruit (seed) of *Carum Carvi*. It is a colourless or pale yellow oil, which gradually darkens in colour on keeping. It has a spicy taste.

Oil of caraway consists essentially of dextro-limonene and carvone, $C_{10}H_{14}O$ (see page 380). Possibly a small amount of carvacrol is also present. It is to the carvone that the value of caraway oil is chiefly due. On this account many of the oils of commerce have been partially or wholly deprived of their carvone,[1] which latter commands a high price, and is official in

sometimes have a specific gravity as low as 0.875 and consist almost entirely of terpenes. This light camphor oil is used to a considerable extent for the adulteration of the more valuable essential oils, such as those of peppermint and eucalyptus.

[1] German "light oil of caraway" is merely the terpene obtained as a bye-product in the manufacture of carvone. It has a specific gravity of about 0.850 and an optical rotation exceeding +100°. It is largely employed in soap perfumery.

certain Pharmacopœias.[1] Such inferior oils can be detected by their lowered specific gravity.

The British Pharmacopœia directs that oil of caraway should have a specific gravity of 0.910 to 0.920. According to Schimmel & Co., normal oil of caraway may have a specific gravity of 0.907 (generally, 0.908 to 0.910). J. C. Umney, however, regards 0.910 as being the lowest allowable limit.

According to the investigations of Schimmel & Co., the oil from the young caraway plant is rich in limonene, but poor in carvone. From the riper material, an oil richer in carvone and poor in limonene is obtained. These observations go to show that the terpene is first formed in the plant, and that the oxygenated constituent is subsequently produced from the terpene.

The optical rotation of oil of caraway is not stated in the British Pharmacopœia (1898), though the U. S. Pharmacopœia (8th Rev.) gives the limits +70° to +80° at 25° C. The rotation of pure oils ranges from about +70° to +85°, the mean of these figures being the average rotation of the oil.

Caraway oil is soluble in an equal volume of alcohol (90 per cent. by volume), and in 3 to 10 volumes of 80 per cent. alcohol (U. S. Pharmacopœia).

A useful method for the valuation of oil of caraway is the fractional distillation of the oil. Genuine oils will show the largest fractions between 170° and 180° C. (which contains the whole of the limonene and should not exceed 25 per cent.) and 220° and 230° C. (which contains the carvone, and should not be less than 40 to 50 per cent.). At least 40 per cent. of oil of caraway should distil above 200° C.

The presence of a fair amount of carvone in caraway oil may be detected by heating equal parts of the oil and phenyl-hydrazine for a few minutes to 100°, when on cooling the mixture, a mass of light yellow crystals of the *hydrazone*, $C_{10}H_{14}$:N.NH.C_6H_5, will be produced.

Cedar-wood Oil.

This oil is obtained from several varieties of cedar, but the oil commonly known under this name, the oil of red cedar-wood, is prepared by the distillation of the wood of *Juniperus virginiana*.[2] The supply comes from many parts of North America,

[1] Pure carvone has a specific gravity of 0.963 to 0.966. Commercial "carvone" is often sold having a specific gravity from 0.933 to 0.944. It is thus merely fractionated caraway oil. Schimmel & Co. have noted the presence of alcohol (about 5 per cent.) in such samples of commercial "carvone."

[2] An oil distilled from the wood of *Cedrus atlantica* (Atlas Cedar Oil) by Schimmel & Co. was found to have sp. gr. of 0.9517; optical rotation, +48.25°; solubility in 90 per cent. alcohol, 1:3 or 4. The oil contained about 17 per cent. of an alcohol (cedrol ?), $C_{15}H_{26}O$.

and the oil is usually distilled from the waste wood-shavings from the manufacture of lead-pencils. A much inferior oil is sometimes prepared from the condensed vapours of the drying chambers containing the cedar-wood, but the product is devoid of the good odour and other properties of the true cedar-wood oil.

Oil of cedar-wood is a colourless, yellow, or often brownish, thickish oil, with a mild persistent odour. The specific gravity ranges from about 0.940 or 0.945 to 0.960. Cedar-wood oil is always lævo-rotatory, its optical rotation varying from —25° to —40° in a 100 mm. tube. It has a high refractive-index (about 1.505 at 17° C.), and for this reason is much used in connection with oil-immersion lenses.

The oil is soluble in alcohol with difficulty, requiring usually from 10 to 20 parts of 90 per cent. alcohol for solution.

Cedar-wood oil, when distilled from very old wood, contains a considerable quantity of *cedrol*, or cedar-camphor.[1] Schimmel & Co. do not consider that this constituent is an essential one in normal cedar-wood oil, but that it is formed when the oil is kept under certain conditions. Whether this is so has not yet been definitely decided, but only small amounts of cedrol are present in the normal oil of cedar-wood.

Besides cedar-camphor, there are present in this oil the sesquiterpene cedrene (see page 276), and possibly also cadinene.

Good samples of cedar-wood oil should not contain more than about 10 per cent. of the crystalline cedrol (cedar-camphor). Parry obtained, by the examination of four genuine samples, 2.32, 2.21, 2.13, and 1.72 per cent. of KOH required for the saponification of the acetylated oils. The results are somewhat low, owing to the dehydrating action of the acetic anhydride used in the acetylation.

Cedar-wood oil is largely used as an adulterant of sandal-wood oil. It may be detected and determined as described on page 469. Cedar-wood oil, in addition to its employment with oil-immersion lenses, is also used in soap-perfumery, &c.

Adulteration of this oil is not very frequent. Pure cedar-wood oil may be known by its specific gravity, high lævo-rotatory power, and by the saponification values of the oil before and after acetylation.

The following table gives the chief characters of the less important cedar-wood oils of commerce.[2] Oil of Jamaica or Honduras cedar is in reality not a cedar oil, and is more correctly termed "cedrela oil." It is, however, conveniently included in

[1] CEDROL, $C_{15}H_{26}O$, was obtained from cedar-wood oil, so long ago as 1841, by Walter (*Liebig's Annalen*, xxxix, p. 247). It forms, when pure, silky crystals with a pleasant aromatic odour. It melts at 78° to 80° C.

[2] The figures given in the table have been taken mainly from Schimmel & Co.'s *Reports*.

this table. Many others of these oils are most probably obtained from the wood of *Cedrela* species:—

OIL.	SOURCE.	SPECIFIC GRAVITY.	OPTICAL ROTATION°. 100 MM.	CHARACTERS AND CONSTITUENTS.
Cedar-wood, Lebanon,.	Wood of *Cedrus Libani.*	0.985	—10.8	Brownish-yellow oil of pleasant odour.
Cedar-wood, Corinto,...	Unknown.	0.906	—17.3	Yellow oil.
Cedar-wood, Cuba,.....	Unknown.	0.923	+18.1	Yellowish oil, containing cadinene.
Cedar-wood, La Plata, .	Unknown.	0.928	Inactive.	Bright blue colour.
Cedar-wood, Costa Rica,	Unknown.	0.915	—5.9	Yellow oil, consisting chiefly of cadinene.
Cedrela (Jamaica Cedar-wood),[1].............	*Cedrela odorata.*	0.935	About —1	

CEDAR-LEAF OIL.

This oil should, presumably, be obtained by the distillation of the leaves of the red cedar, *Juniperus virginiana.* This is, however, not the only source of the oil, since other leaves, such as *Thuja occidentalis,* are also undoubtedly used in its preparation. Many conifers in North America pass under the name of "cedar"; thus *Thuja occidentalis,* and *Chamæcyparis sphæroidea* are termed "white cedar."

The true cedar-leaf oil, from *J. virginiana,* is rarely found on the market. It is an oil having a pleasant, sweetish odour. Gildemeister and Hoffmann (*The Volatile Oils*) state that this oil has a specific gravity of 0.887, and an optical rotation of +59.4°. It is insoluble in 16 parts of 80 per cent. alcohol. A large portion of the oil distils below 180° C., of which the greater part comes over between 173° and 176° C. This fraction consists of dextro-limonene. Other terpenes are also present, including, probably, pinene. Cadinene is contained in the higher fractions, while borneol and bornyl esters (including probably bornyl valerate) are also present in the oil.

The following analyses of commercial oils show the differences existing between them and pure oil of cedar-leaf (*Schimmel's Report,* April, 1898, p. 14):—

SPECIFIC GRAVITY.	OPTICAL ROTATION°. (100 MM. TUBE.)	SOLUBILITY IN 70 PER CENT. ALCOHOL.
0.897	—12.4	Insoluble.
0.886	— 3.7	Insoluble.
0.887	—24.2	Insoluble.
0.920	—10.4	1 in 4.
0.918	—11	1 in 5.
0.905	—10	Insoluble.

[1] This forest tree is a native of the Caribbee Islands and of Barbadoes. It has an odour resembling the true cedar, and is thus frequently called Jamaica or Honduras cedar. The greater part of the cigar boxes made are manufactured from the wood of this tree.

All these samples contained more or less oil of thuja, as was evident from their odour.

Commercial oil of cedar-leaf is thus usually obtained by the distillation of miscellaneous conifer-needles, including those of thuja. Red thuja oil is sometimes met with under the name "cedar oil." The true cedar-leaf oil is much more valuable than either cedar-wood oil, or the oils from thuja and other varieties of conifers.

Chamomile Oils.

Chamomile oil occurs in commerce in two varieties, namely, Roman Chamomile oil and German Chamomile oil. The former is the oil distilled from the flowers of *Anthemis nobilis;* the latter is obtained from the flowers of *Matricaria chamomilla.*

ROMAN CHAMOMILE OIL is official in the British Pharmacopœia (1898), which describes it as a pale blue or greenish-blue oil when freshly distilled, gradually becoming yellowish-brown. It has the aromatic taste and odour of the flowers. The specific gravity of the oil ranges from 0.904 to 0.916 at 15° C., and it is only slightly optically active (+1° to +4°).

Roman chamomile oil is remarkable for the number of compounds of the aliphatic series which occur in it. These compounds include isobutyl isobutyrate and angelate; amyl tiglate[1] and angelate; hexyl tiglate[2] and angelate; and *anthemol*, $C_{10}H_{16}O$, as was shown by the researches of Demarcay. Naudin (*Bull. Soc. Chim.*, xli, p. 483) also isolated a hydrocarbon of the olefine series, which contained $C_{18}H_{36}$ and was termed by him *anthemene*. It crystallises in needles melting at 63° C.

There are no recognised methods for the analysis of chamomile oil. The odour, &c., as described by the Pharmacopœia, should be noted. This is characteristic, both in the case of Roman and German chamomile oils. Doubtful samples should be submitted to a comparative test with a specimen of the pure oil. The

[1] According to Blaise (*Bull. Soc. Chim.*, 1903, p. 327), Roman chamomile oil does not contain any compound of tiglic acid, the small quantities usually found being due to the action of alkali on the angelic acid on saponification. Angelic acid forms 80 per cent. of the total acids in the oil.

[2] *Angelic* and *tiglic acids* are stereo-isomers, having the empirical formula $C_5H_8O_2$. They are unsaturated acids of the acrylic series, and their constitution is shown by the following formulæ:—

ANGELIC ACID.	TIGLIC ACID.
$CH_3.CH$	$CH_3.CH$
$\Vert$	$\Vert$
$CH_3.C.COOH$	$COOH.C.CH_3$

Angelic acid melts at 45° C., while tiglic acid melts at 64.5° to 65° C.

specific gravity of the Roman chamomile oil should come within the limits specified above.

Chrysanthemum Oil, distilled from the green leaves of *Chrysanthemum japonicum* (the autumn chrysanthemum), is considered by G. Perrier to resemble the oil of Roman chamomile. The yield is about 0.16 per cent. of a green oil having an odour of peppermint and chamomile. Chrysanthemum oil begins to boil at 160° C., and has a specific gravity of 0.932 at 15° and a refractive index of 1.4931 at 18°. It is soluble in ten volumes of 95 per cent. alcohol, but nearly insoluble in alcohol of 70 per cent. When cooled to a very low temperature, the oil solidifies. It contains an aldehydic substance which combines with sodium bisulphite, and it apparently also contains angelic acid.

GERMAN CHAMOMILE OIL is a blue oil, the colour changing gradually by the influence of light to green, and finally brown. Its specific gravity at 15° C. is 0.930 to 0.945. In 1871, it was found by Kachler to contain an acid which has since been identified as *caprinic acid.* Schimmel & Co. state that the average saponification-number of the oil is 45, so that it is highly probable that the oil contains a notable quantity of esters.

German chamomile oil, when cooled to a low temperature, becomes a semi-solid mass of the consistency of butter. Schimmel & Co. (*Report,* April, 1894) have shown that this behaviour is due to the presence of a paraffin or mixture of hydrocarbons. This buttery substance dissolves with difficulty in alcohol; but it is readily soluble in ether, and persistently retains the blue colour of the oil.[1] When quite pure, it is said to be a brilliant white body melting at 53° to 54° C., showing all the properties of a paraffin.

German chamomile oil of commerce is said to be sometimes adulterated with oil of milfoil, and with cedar-wood oil. Oil of milfoil is a blue oil, but as its odour is quite different from that of chamomile oil, it would be impossible to add it in any quantity without detection. Chamomile oil adulterated with an appreciable quantity of cedar-wood oil remains liquid at 0° C. (Schimmel & Co.), whereas the genuine oil begins to thicken at 15° and congeals at +1° C. The oils of copaiba, lemon, and turpentine are also used as adulterants of chamomile oil.

Clove Oil.

Clove oil is obtained by distillation from the buds and stems of *Eugenia caryophyllata.*[2] It has the characteristic odour of

[1] The body to which the oil owes its blue colour is unknown.

[2] A cheap and inferior oil is made from the *stalks* of the clove-plant. It appears to contain no acetyl-eugenol.

cloves, and a pungent taste. When freshly distilled the oil is colourless, or faintly yellow, but the colour deepens on keeping. Clove oil is soluble in about 60 parts of proof spirit, and dissolves in rectified spirit and glacial acetic acid in all proportions. The oil is also soluble in about 2 volumes of 70 per cent. alcohol. The specific gravity varies from not less than 1.050 to 1.068. Any sample with a lower gravity than 1.050 is adulterated or suspicious.[1] The optical activity of clove oil varies from 0° to —1°, and the boiling-point should not be below 245°. The refractive index of the oil is an additional guide to its purity, the index of eugenol itself being 1.5412 at 20° C. (W. H. Simmons).

The chief and most important and abundant constituent of clove oil is the phenoloid body, eugenol, $C_{10}H_{12}O_2$, the proportion ranging from 80 to 95 per cent. The greater part of the eugenol is free, but there exist in clove oil esters of eugenol (chiefly acetate) in amount ranging from 7 to 17 per cent. The sesquiterpene, caryophyllene, makes up the greater part of the remaining portion of the oil.[2] Jorissen (*Pharm. Jour.*, 1893, p. 261) states that oil of cloves contains traces of a substance resembling or identical with vanillin, which possibly has its origin in the oxidation of eugenol. Heine & Co. state that traces of naphthalene are present in clove oil. Schimmel & Co. have found methyl-alcohol, furfurol, and traces of an aldehyde (not acetaldehyde). They consider that the darkening of oil of cloves is probably partly due to the presence of furfurol.

Erdmann has observed the presence in clove oil of salicylic acid, probably combined as eugenol acetyl-salicylate. The same worker also confirmed Schimmel & Co.'s observation of the presence of furfurol in the preliminary distillate of cloves.

The British Pharmacopœia (1898) states that oil of cloves should have a specific gravity of not less than 1.050, and that the alcoholic solution should yield a blue colour with ferric chloride. When shaken with its own volume of ammonia, clove

[1] E. J. Parry states, however, that a sample examined by him, which was an absolutely pure oil guaranteed by one of the most reputable drawers in England, had the low specific gravity 1.0494 at 15.5° C. It contained 84 per cent. of eugenol as determined by Umney's potash absorption method, and answered to the B. P. tests in all other particulars. Parry suggests 1.048 as the minimum limit for the specific gravity of the oil. Schimmel & Co. consider the limits of 1.045 to 1.070 to be compatible with genuine oils.

[2] Schimmel & Co. (*Report*, April, 1897, p. 45) have isolated from clove oil a very small quantity of a body which appears to be normal amyl-methyl-ketone, $C_5H_{11}.CO.CH_3$. This is believed by them to be the other odoriferous constituent of the oil, as it imparts to a mixture of eugenol and caryophyllene a clove-like odour, even when added only in traces. More recently, the discovery of methyl-heptyl-ketone and methyl benzoate in clove oil has been announced (*Reports*, 1902 and 1903, April).

oil should form a semi-solid yellowish mass due to the presence of eugenol.[1]

Alcohol is occasionally added as an adulterant to oil of cloves. It lowers the characteristically high specific gravity of the oil, and begins to distil over below 100°, whereas pure clove oil will yield *no* distillate below 245° C.

Petroleum and oil of turpentine are sometimes used as adulterants of oil of cloves. Such sophistications can readily be detected by the decreased solubility of the oil in 90 per cent. alcohol.

The cheaper kinds of German clove oil are specially liable to have suffered a partial abstraction of eugenol, or to be composed of a mixture of pure oil with the residue (caryophyllene) from the manufacture of eugenol. Such oils have a low specific gravity, and are less soluble in 90 per cent. alcohol than pure oil of cloves. The eugenol-content will, of course, be also lessened.

An oil which was said to be used in certain German works as an adulterant of oil of cloves was found by E. J. Parry to consist of pure cedar-wood oil. Such an adulterant would lower the specific gravity of the oil, whilst it would render it less soluble in 90 per cent. alcohol. It would also increase the lævo-rotation.

The various methods for the determination of eugenol in clove and other oils are described on page 361. According to E. C. Spurge (*Pharm. Jour.*, 1903, ii, 701; 757), the determination of the eugenol by Umney's method (uncorrected), together with the observation of the specific gravity, is sufficient for a Pharmacopœia test. The U. S. Pharmacopœia requires clove oil to contain at least 80 per cent. of eugenol when assayed by Umney's method (p. 361), 10 c.c. of the oil being employed with 100 c.c. of 5 per cent. caustic potash, with which latter solution, also, the liquid is brought to the zero-mark in the flask.

Coriander Oil.

Coriander oil is distilled from the fruit of *Coriandrum sativum*. It is a colourless or pale yellow oil, having an odour and flavour of the fruit.

The British Pharmacopœia (1898) directs that the oil should have a specific gravity of 0.870 to 0.885, and that 1 c.c. of the oil should yield a clear solution with 3 c.c. of 70 per cent. alcohol.

[1] Unless the proportion of ferric chloride be very small, a bright green colour is produced. After shaking 1 part of the oil with 20 parts of *hot* water, and filtering the aqueous liquid, the latter should not give a blue coloration with ferric chloride (absence of phenol), though a transient grey-green colour may be produced (U. S. Pharmacopœia).

The latter test shows the absence of oil of turpentine and added terpenes.

The constituents of coriander oil have not been very thoroughly studied. Pinene is undoubtedly present. The alcohol found by Semmler and termed by him "coriandrol," has been proved by Barbier (*Compt. rend.*, 1893, p. 1459) to be dextro-linalol, $C_{10}H_{18}O$. This is the chief constituent. The body to which oil of coriander owes its characteristic odour has not yet been isolated.

Oil of coriander differs in its composition according as it has been obtained from ripe or unripe fruits. The oil from the ripe fruit answers to the British Pharmacopœia limits. Schimmel & Co. have investigated the nature of the oils distilled from the fruit, &c., at various periods of its growth. The results are shown in the following table:—

Nature of Material.	Specific Gravity at 15.5° C.	Optical Rotation°. (100 mm.)	Solubility in 70 per cent. Alcohol.	Remarks.
1. Oil from the entire flowering plant (green), ...	0.853	....	Insoluble.	Objectionable bug-like odour which had almost entirely disappeared after 2½ months.
Same, after keeping 2½ months, ..	0.856	+1.03		
2. From green half-ripe herb with fruits, ...	0.866	+7.2	1 : 3	Odour of coriander with slight bug-like odour.
Same, after keeping 1 month, ...	0.869	....	....	Pure coriander odour.
3. From ripe coriander fruit, ...	0.876	+10.8	1 : 3	....

The optical rotation of oil of coriander is not stated in the British Pharmacopœia. It varies from +6° to +15° in a 100 mm. tube (U. S. Pharm., +7° to +14°).

The chief constituent of the oil being linalol, a large fraction (about 45 to 50 per cent.) should distil at 190° to 200° C.

Orange oil, turpentine oil, and the oils of cedar-wood and cubebs have been used as adulterants of coriander oil. The two first-named will be detected by the increase in the optical rotation, and also by the lowering of the specific gravity. The reverse effects will be produced by the addition of oils of cedar and cubebs.

Cubebs Oil.

This oil is obtained by the distillation of the unripe dried fruit of *Piper cubeba*. It is usually of a greenish or greenish-blue colour (occasionally greenish yellow), and has the characteristic camphoraceous odour and flavour of cubebs.

The British Pharmacopœia (1898) states that the specific gravity of the oil ranges from 0.910 to 0.930, but most samples of genuine oil of cubebs have a gravity of 0.920 to 0.930. The optical rotation is not stated, but it ranges between —25° and —40° (average about —30°), the lower limit being that given by Gildemeister and Hoffmann (*The Volatile Oils*), and adopted in the U. S. Pharmacopœia (8th Rev.), which gives —25° to —40° for 100 millimetres.

The constituents of this oil have not as yet received much attention. One or more terpenes (including dipentene and probably pinene or camphene), and two sesquiterpenes (including cadinene), exist in the oil. Besides these, a sesquiterpene alcohol of the formula $C_{15}H_{25}OH$ is present, especially in the case of oils distilled from old oxidised fruits. This body is the so-called "*cubeb-camphor.*" It crystallises in rhombic prisms melting at 65° to 67° (or, according to Winckler, at 70°) and boils at 245° to 248° C., with partial decomposition.

The oil begins to boil at about 175° and distils mainly between 250° and 270° C. A genuine oil on fractional distillation gave the following results:—Below 250°, 9 per cent.; 250° to 260°, 27; 260° to 270°, 48; 270° to 280°, 7; above 280°, 9 per cent.

The higher fractions of oil of cubebs have an intensified blue colour, which character has been erroneously ascribed to the presence of copper. The body or bodies causing the coloration are unknown.

Oil of cubebs is now rarely adulterated, owing to its low price. The presence of turpentine oil would be revealed on fractionation. Genuine oil of cubebs is soluble in 1 to 2½ parts of 90 per cent. alcohol.

Cumin Oil or Cummin Oil. Roman Caraway Oil.

This oil is obtained by the distillation of the fruit from *Cuminum cyminum*. It is an almost colourless or light yellow oil, with a characteristic smell of cumin and a bitterish taste. The oil of commerce is chiefly obtained from the fruits grown in Sicily, Malta, and India.

The oil from the fruit obtained in the Levant has a specific gravity of 0.910 to 0.930; Indian oil has a slightly lower specific

gravity, 0.893 to 0.899. The optical rotation of these oils varies from +4° to +8° in a 100 mm. tube.

Oil of cumin is fairly soluble in 80 per cent. alcohol. The solubility of the oil depends upon the amount of cumic aldehyde present, oils of a high gravity (containing much of this heavy constituent), being soluble in three parts of 80 per cent. alcohol, and lighter oils requiring as much as 10 parts of 80 per cent. alcohol.

The oil contains a *terpene*[1] which has not yet been identified; cymene; and cumic aldehyde ("cuminol"), $C_{10}H_{12}O$.[2] The last-named constituent may be isolated and determined in the following way (Kraut, *Annalen*, xcii, p. 66):—The terpenes of the oil are removed by distillation, only the portion boiling above 190° C. being reserved for further treatment. This high-boiling fraction is next shaken with sodium bisulphite solution, the resultant crystalline mass being pressed after standing for twenty-four hours. The crystals are then washed with a mixture of alcohol and ether, and distilled with a solution of sodium carbonate. (See table on p. 251.)

Dill Oil.

This oil is distilled from the fruit of *Peucedanum graveolens*. The colour of the oil is pale yellow, having an odour of the fruit and a sweet and aromatic taste. The British Pharmacopœia (1898) requires dill oil to have a specific gravity of 0.905 to 0.920 at 15.5°. It should have an optical rotation of not less than +70° in a 100 mm. tube.

The constituents of the oil of dill comprise carvone, *d*-limonene, phellandrene (stated by Schimmel & Co. to be present in English and Spanish oils), a paraffin-hydrocarbon, and "dill-apiol" (in Indian dill oil, which is the product of *Anethum Sowa*). This substance is isomeric with "apiol," present in oil of parsley.[3]

[1] Wolpian (*Pharm. Zeit. Russ.* (1896), xxxv, p. 97) isolated this terpene which he found to have a boiling-point of 157° to 158° C., sp. gravity 0.8604, and an optical rotation of +25.4°. To this he gave the name "hydrocuminene." There is as yet, however, insufficient evidence for assuming this body to be a distinct and hitherto unknown chemical individual.

[2] It has been pointed out by Gildemeister and Hoffmann that if cumic aldehyde is a true aldehyde, the name "cuminol" is incorrect, and should be "*cuminal*."

[3] Dill-apiol, like its isomer apiol, is converted by the action of alcoholic potash into an isomeric product, by an alteration of the allyl- to the propenyl-group. Dill-apiol is a thick, oily liquid, with a boiling-point of 285° C. *Iso*-dill-apiol, formed by the action of alcoholic potash, is a body forming colourless prisms melting at 44°, and boiling with slight decomposition at 296° C. Bromine forms a tribromo derivative with both apiol

Oil of dill thus resembles caraway oil in composition, but it contains less carvone than the latter oil. The odours of the two oils are quite different.

Oil of dill differs in character according to its origin. J. C. Umney (*Pharm. Jour.*, 1897, March 13; 1897, 556; 1898, 176) has pointed out the differences between the oil obtained from English fruits and that from Indian dill fruit. Indian oil of dill has a higher specific gravity and a smaller carvone-content than the English oil. The following results were obtained by Umney on five samples of oil of dill. The Japanese oil resembles Indian dill oil in its characters:—

Oil.	Specific Gravity.	Optical Rotation (100 mm.)	Fractional Distillation.				
			Below 200° C. (Per cent.)	200–210° (Per cent.)	210–220° (Per cent.)	220–230° (Per cent.)	Above 230° C. (Per cent.)
English,	.9148	+72.25°	22	14	12	50	2
English,	.9146	+80.25	21	19	12	46	2
German,	.9002	+70.25	53	13	12	17	5
Indian,	.9486	+47.5	24	17.5	7	10.5	39
Japanese,	.9643	+50.5	21	12	10	8	49

German oil of dill is similar to English dill oil, but Umney considers that the above sample of German dill oil has suffered partial deprivation of its carvone.[1] Schimmel & Co. state that although the specific gravity of this sample is somewhat low, yet it is quite consistent with a pure oil. They record eight examples of oils of Thuringian dill with specific gravities ranging from 0.899 to 0.911.

and dill-apiol. The differences between the two classes of compounds are shown in the following table (compare page 364):—

	From Parsley Oil.		From Dill Oil.	
	M. Pt., ° C.	B. Pt., ° C.	M. Pt., ° C.	B. Pt., ° C.
Apiol,	30	294	Liquid	285
Iso-Apiol,	55 to 56	303 to 304	44	296
Bromapiol dibromide,	88 to 89	..	110	..
Brom-isoapiol dibromide,	120	..	115	..
Apiolic aldehyde,	102	..	75	..
Apiolaldoxime,	160 to 161	..	..	..
Apiol-acet-aldoxime,	128 to 129	..	..	..
Apiolic acid,	175	..	151 to 152	..
Apione,	79	..	..	..
Dibromapione,	99 to 100	..	..	..

[1] E. J. Parry (*Chemistry of Essential Oils, &c.*) concurs with Umney's statement as to the probable abstraction of carvone from dill oil having a specific gravity below 0.905 at 15.5° C.

The physical constants for oil of dill are the most reliable criteria on which to judge of the quality of a sample. The specific gravity should lie between 0.910 and 0.925, and the optical rotation (for 100 mm.) should be from +70° to +85°. These figures should be taken as maximum and minimum limits. Fractional distillation is valuable as a method for the approximate determination of carvone. Not more than 15 to 20 per cent. of the oil should distil below 185° C., and at least 35 to 40 per cent. between 185° and 225° C. E. J. Parry states that not less than 40 per cent. should distil above 220°.

In order to exclude the apiol-containing oil from Asiatic fruits, the official characters of the oil (*Oleum Anethi*) should be adhered to (Umney).

Eucalyptus Oils.

The oils distilled from the leaves of the many species of *Eucalyptus* (*Myrtaceæ*) differ so greatly in their physical characters and chemical composition that no sufficient indication is afforded of the nature of the oil unless the species of eucalyptus is stated.

The constituents of the various oils of eucalyptus include dextro- and lævo-pinenes (the former of which was at first termed "eucalyptene"); phellandrene; probably camphene and fenchene; the sesquiterpene aromadendrene; cineol (eucalyptol); citronellal; citral; cuminal(?);[1] citronellol; geraniol; geranyl acetate, and various aldehydes and esters; and the stearoptene eudesmol (p. 423). The oils which are valued in medicine contain cineol as their chief constituent. The official oil of the British Pharmacopœia (1898) is that from *E. globulus*,[2] which usually contains at least 50 to 60 per cent of cineol, and frequently up to 80 per cent., together with pinene and traces of ethyl alcohol, amyl alcohol, and butyric, caproic, and valeric aldehydes. The oil is much used as a preventive of influenza. Cases of poisoning by ingestion of the oil have occurred.

The official oil (from *E. globulus*) is the most valued in medicine. The oils from *E. cneorifolia*, *E. dumosa*, *E. leucoxylon*, *E. oleosa*, *E. punctata* and *E. Morrisii* resemble that from *E. globulus* very closely in physical characters and chemical composition, and therefore frequently comply with the requirements

[1] According to H. G. Smith, the aldehyde occurring in a large number of eucalyptus oils is not cumic aldehyde, as hitherto supposed, but a new aldehyde to which he gives the name aromadendral (p. 423).

[2] The British Pharmacopœia (1885) recognised the oils from *E. globulus*, *E. amygdalina*, and other species of eucalyptus.

of the British Pharmacopœia.[1] A eucalyptus oil answering to these requirements is a "colourless or pale yellow oil, having an aromatic camphoraceous odour and a pungent taste, leaving a sensation of coldness in the mouth. Specific gravity, 0.910 to 0.930.[2] It should not rotate the plane of a ray of polarised light more than 10° in either direction in a tube 100 mm. long, and it should become semi-solid on being stirred, when cold, with a third or half its volume of phosphoric acid of commerce of specific gravity 1.750 (presence of a due proportion of cineol). If to 1 cc. of the oil there be added 2 cc. of glacial acetic acid and 2 cc. of a saturated aqueous solution of sodium nitrite, the mixture, when gently stirred, should not form a crystalline mass (exclusion of eucalyptus oils containing much phellandrene)." This last-named test is included in the U. S. Pharmacopœia.

The specific gravity of the oils of eucalyptus varies from 0.850 to 0.930 at 15° C. The lower figure is only reached in the case of the oil from the leaves of *E. amygdalina*, which is largely composed of phellandrene, with very little cineol. The other oils range in specific gravity from 0.870 to 0.930. Oils rich in phellandrene have a low specific gravity, whilst those having a high cineol-content approach the higher limit, 0.930, which is the specific gravity of pure cineol.[3]

The optical rotation of the oils of eucalyptus is as variable as the specific gravity. This is only to be expected, since some oils contain much of the inactive cineol, while others consist mainly of phellandrene, which has a very high optical rotation. The official oil is limited in its optical rotation from +10° to —10° in a 100 mm. tube. Oils between these limits of optical

[1] It has been pointed out by W. J. Brownscombe (*The Lancet*, No. 3940, p. 632) that eucalyptus oils other than *E. globulus* often answer the B. P. tests, whilst some globulus oils do not respond to all the official requirements. Amongst the oils which have a fairly high cineol content, and yet do not exactly conform to the tests of the Pharmacopœia, are those from *E. eugenoides*, *E. macrorrhyncha*, and *E. odorata*. The last-named contains a notable amount of phellandrene.

[2] Some authorities have suggested that the minimum specific gravity of the B. P. oil might preferably be fixed at 0.905. Oils having a cineol content of 45 to 52 per cent. and answering to the pharmacopœial requirements in every other respect, have been found to have specific gravities ranging from 0.906 to 0.910 at 15° C. The author has examined pure samples ranging in gravity from 0.907 to 0.930. The B. P. limits are preferable, as they tend to keep up the cineol-content.

[3] It is not to be assumed, however, that any eucalyptus oil of specific gravity near 0.930 is necessarily composed mainly of cineol. The researches of Baker and Smith (*Proc. Roy. Soc.*, New South Wales) have shown that eudesmol and other high-boiling constituents of the oil of certain species of eucalyptus have high specific gravities. Thus an oil containing a large proportion of eudesmol and a small amount of cineol will have a high gravity.

activity and of the correct specific gravity will contain a proper percentage of cineol. The determination of the optical rotation of the oil is not of much value. The U. S. Pharmacopœia requires eucalyptus oil to be *dextro-rotatory*, up to +10°.

A pure sample of globulus oil examined by the author showed a refractive index of 1.4642 at 25° C. The refractive index of pure cineol is said to be 1.4596 at 17° C.

The most convenient test for the presence of phellandrene is based on the formation of *phellandrene nitrite*, $C_{10}H_{16}N_2O_3$. If much phellandrene is present, a crystalline mass of this compound will be produced when the oil is mixed with glacial acetic acid and sodium nitrite solution. A sample of eucalyptus oil purchased under the Sale of Food and Drugs Acts, and examined by A. R. Tankard in the author's laboratory, had a specific gravity of 0.8897, contained little or no cineol, but much phellandrene. It had a refractive index of 1.4830 at 25°.

It has been shown by H. G. Smith (*Chemist and Druggist*, 1899, p. 534) that certain eucalyptus oils are dextro-rotatory when they contain the maximum amount of cineol, and that they do not then contain phellandrene, though this constituent may be present at certain times of the year.

According to Baker and Smith (*Chemist and Druggist*, 1899, 299) the emerald-green colour given by eucalyptus oils with the pharmacopœial nitrite test is not due to phellandrene, but to the pinenes present. Oils in which dextro-pinene is predominant are stated to give the colour to a more marked degree than those which contain an excess of lævo-pinene. Turpentine oil gives a brilliant green coloration. A pure sample of *E. globulus* examined by Baker and Smith gave only a dull green colour with the nitrite test. The oil from *E. microcorys*, which consists very largely of dextro-pinene with some cineol, but contains no phellandrene, is stated by Baker and Smith to give a beautiful green colour. It is worthy of notice that an oil containing no cineol may give a more pronounced green coloration than a pure oil.

The phellandrene test and the determination of the percentage of cineol are the most useful data on which to judge the quality of oils of eucalyptus. The British Pharmacopœia test for the presence of a due content of cineol is much too indefinite, but the U. S. Pharmacopœia method of assay is sufficiently accurate for most purposes (see p. 422). Unfortunately, a completely satisfactory method for the determination of cineol has not yet been described. The methods in use are generally based upon some modification of the phosphoric acid process.[1] It was first

[1] According to H. G. Smith (*Chem. News*, 1902, lxxxv, 3) the pink coloration observed with some eucalyptus oils when examined by the phosphoric acid test is due to the presence of a sesquiterpene, named by

pointed out by L. R. Scammel (*Brit. Patent*, 1894, No. 14,138) that by the addition of concentrated phosphoric acid (sp. grav. 1.75 to 1.785, preferably the latter) in slight excess to the cineol-containing oil at a temperature not exceeding 60° F., the whole of the cineol is thrown down in the form of the crystalline phosphate. The cineol phosphate may then be treated in several ways. Thus it may be thoroughly pressed between blotting-paper, and the cake of phosphate weighed; or it may be decomposed with water (cold), and the free cineol weighed[1] (as recommended by Scammel, who, however, used *hot* water); or the solution of cineol phosphate in water may be titrated, and the cineol calculated from the phosphoric acid indicated, assuming that one molecule of phosphoric acid is equivalent to one molecule of cineol.

With regard to the weighing of the pressed cake of cineol phosphate, D. B. Dott (*Pharm. Jour.*, 1899, i, 57) states that in order to ensure the absence of terpenes and uncombined acid from the phosphate, it is essential to press the mass repeatedly between folds of blotting-paper. This requires some time, and there is risk of the absorption of water by the hygroscopic compound, thus causing error. The second method of procedure, that of weighing the free cineol after the decomposition of the phosphate compound with cold water, is held by Dott to be very liable to give a result in excess of the truth, since the free cineol often contains a considerable quantity of undecomposed phosphate in solution. On the other hand, if *hot water* or sodium carbonate solution be used to decompose the phosphate, loss may result owing to solution of the free cineol.[2]

The third method, namely, that of titrating the phosphoric acid combined with the cineol, is preferred by Dott to the weighing of the pressed compound or of the free cineol. Too great an excess of phosphoric acid must be avoided. This is best done by determining approximately the amount of cineol present, and then making another determination with only a slight

him *aromadendrene*. This hydrocarbon occurs in large amounts in the oil from *E. hæmastoma*. Aromadendrene boils at 260° to 265°, and has a specific gravity of 0.925 at 19°. When the vapour of bromine is allowed to fall on its solution in glacial acetic acid, aromadendrene gives a crimson colour, which quickly changes to violet and finally to a deep indigo-blue.

[1] E. J. Parry (*Chemistry of Essential Oils, &c.*) states that in his opinion this process, when carefully worked, gives results accurate to 3 per cent. when the oil contains at least 30 per cent. of cineol. If the cineol-content is lower than this, the oil must be previously fractionated. Faulding (*Chemist and Druggist*, 1895, p. 310) also states that the cineol is quantitatively separated by Scammel's process.

[2] Dott has pointed out that cineol is much more soluble in diluted phosphoric acid than in water.

excess of phosphoric acid. L. F. Kebler recommends the following procedure (*Amer. Jour. Pharm.*, 1898, lxx, p. 492):—8 grammes (or less) of the oil in a beaker is cooled in ice-water, 4 cc. of phosphoric acid solution (sp. gr. 1.75) added, and the mixture again placed in ice-water. When cool, the contents of the beaker are slowly and thoroughly mixed with a glass rod, the cineol phosphate separated, pressed, weighed, and decomposed with hot water.[1] The acid is then titrated with a standard potassium hydroxide solution. According to the cineol-content of the oil, it is occasionally necessary to add more than the specified quantity of phosphoric acid. Kebler obtained, by working on pure cineol, a result showing 103.75 per cent. Fair approximations to the truth are thus obtained, the process being easy and rapid. D. B. Dott thinks it probable that as water decomposes the phosphate compound, better results would be obtainable if anhydrous phosphoric acid were used.

Eucalyptus oil has suffered adulteration by abstraction of its active constituent, cineol, and C. T. Bennett has recently recorded an instance of the wholesale sophistication of eucalyptus oil with 20 per cent. of castor oil (*Chemist and Druggist*, 1905, p. 33). The samples had a somewhat low cineol-content, and left a considerable amount of viscous residue on distillation. This residue required a large proportion of caustic potash for saponification and glycerin was present in the liquid. Castor oil was detected by the usual tests. The presence of this adulterant is likely to be overlooked unless special tests are applied.

In addition, substitution of the valuable cineol-containing official oil of eucalyptus by the medicinally worthless oil from *Eucalyptus amygdalina*,[2] has formed the basis of several prosecutions.

The valuable researches of Baker and Smith (*Jour. Roy. Soc.*, N. S. Wales, 1898; 1900: *A Research on the Eucalypts*, &c.) have revealed the presence of several new compounds in eucalyp-

[1] W. H. Allen (*Chem. and Druggist*, 1899, liv, p. 641) employs *warm* water for the decomposition of the phosphate compound, and finally washes the liberated cineol with warm water to remove any adhering traces of phosphoric acid.

This process with slight modification has been adopted in the U. S. Pharmacopœia (8th Rev.):—Ten cc. of the oil (eucalyptus, cajuput) is dissolved in 50 cc. of "purified petroleum benzin" (petroleum-ether, b. pt., 45° to 60° C.) and phosphoric acid added to the ice-cold liquid drop by drop with constant stirring until the cineol phosphate assumes a yellow or pinkish colour. The precipitate is filtered by means of the pump and washed with cold petroleum-ether. The pressed cake of phosphate is decomposed with *warm* water and the cineol measured. The U. S. Pharmacopœia requires eucalyptus oil to contain not less than 50 per cent. of cineol.

[2] This oil is stated to be a good solvent for rubber.

tus oils. These observers have thoroughly investigated the eucalypts of Australia, and the oils obtained from them, with the result that many oils of eucalyptus of undoubted origin are now known to be quite free from cineol, and to contain large quantities of hitherto unrecognised constituents. The new compounds have all been obtained from the high-boiling fractions of eucalyptus oils, and have a high specific gravity. Amongst them are:—(1) Eudesmol, $C_{10}H_{16}O$, the camphor or stearoptene of certain eucalyptus oils;[1] (2) the amyl ester of eudesmic acid (solid); (3) geranyl acetate, occurring in the oil of *E. Macarthuri* to the extent of 60 to 75 per cent.;[2] (4) aromadendral, $C_{10}H_{14}O$, the aldehyde previously supposed to be cumic aldehyde (although this latter does occur in certain oils); (5) esters, such as those of valeric and acetic acids; and (6) piperitone, a ketone of peppermint odour, occurring in the oils of *E. rossi*, *E. Risdoni*, *E. piperita*, &c.

The amyl ester of eudesmic acid, $C_{14}H_{18}O_2$, is present in the oil from *E. aggregata* to the extent of about 57 per cent., and is apparently a homologue of cinnamic acid. Eudesmic acid is only slightly soluble in cold, but readily soluble in hot water. It forms a dibromide.

H. G. Smith has shown that cineol and eudesmol are nearly allied to one another, since the latter may be converted into cineol by keeping the crude fraction for some time in the presence of oxygen, under suitable conditions. Smith suggests that eudesmol is present at certain times of the year in all oils which are eventually rich in cineol.

The following list comprises the greater number of the best known eucalyptus oils. Fuller information will be found in E. J. Parry's *Chemistry of Essential Oils*, &c., Gildemeister and Hoffmann's *The Volatile Oils*, and in Schimmel & Co.'s *Reports* (see especially *Report* for October, 1904).

[1] EUDESMOL is isomeric with ordinary camphor, and has been found in the oils from *E. capitellata, macrorrhyncha, Smithii, piperita, goniocalyx, camphora*, &c., the last-named oil containing a large amount of this constituent. It is a white solid crystallising in milky needles, melting about 80° C. and boiling at 271°. Eudesmol yields a *dinitro compound* (m. pt., 90°) and a dibromide (56°), but does not form a nitroso-chloride. On oxidation with dilute nitric acid, eudesmol is converted into camphoronic acid, but no camphoric acid is formed.

[2] The oil from *E. Macarthuri*, containing 60 per cent. of geranyl acetate and 10 per cent. of geraniol, together with some eudesmol, but no phellandrene or cineol, differs entirely in appearance, odour, &c., from ordinary commercial oil of eucalyptus. It is always slightly dextro-rotatory. The geranyl acetate present in the oil is completely saponified in the cold by alcoholic potash in 1½ hours, which fact, as pointed out by H. G. Smith, might be utilised in the determination of this constituent in essential oils in the presence of other esters.

Botanical Origin.	Yield, Per Cent.	Specific Gravity at 15° C.	Optical Rotation ° in 100 mm. Tube.	Chief Constituents.
Eucalyptus amygdalina	To 3.5	0.850 to 0.886	—25 to —70	Phellandrene; cineol.
E. Baileyana	1.0	0.890 to 0.940	...	Cineol; citral; phellandrene.
E. cneorifolia	...	0.899 to 0.923	—4 to —14	Cineol; cuminal (?aromadendral).
E. dealbata	3	0.871 to 0.900	...	Citronellal; citronellol.
E. dumosa	1	0.884 to 0.915	+0 to +6.5	Cineol.
E. eugenoides	0.8	0.908	+5	Cineol.
E. globulus	1.5 to 3	0.905 to 0.930	+1 to +10	Cineol; pinene; aldehydes.
E. hæmastoma	2	0.880 to 0.890	...	Cineol; terpenes, including aromadendrene.
E. leucoxylon	1	0.915 to 0.927	+0.5 to +2.7	Cineol.
E. Macarthuri	...	...	slightly +	Geranyl acetate (60%); geraniol; eudesmol.
E. macrorrhyncha	0.3	0.924 to 0.927 at 22° C.	...	Cineol; eudesmol.
E. maculata, var. *citriodora*[1]	1 to 1.5	0.870 to 0.905	To +2	Citronellal (80%); geraniol; citronellol.
E. microcorys	1 to 2	0.896 to 0.935	...	Dextro-pinene; cineol.
E. odorata	1.5	0.899 to 0.925	slightly —	Cineol; cuminal.
E. oleosa	1.25	0.906 to 0.926	+4 to +5	Cineol; cuminal.
E. piperita	0.8	0.909 to 0.913	—3; +1.6	Phellandrene; cineol; eudesmol; piperitone.
E. polybractea (Blue Malee)	...	0.919	—1	Cineol (60%); cuminal (?).
E. punctata	1	0.912 to 0.920	—1 to +4.4	Cineol (45 to 65%).
E. Risdoni	1.35	0.915; 0.916	—5	Cineol; phellandrene; piperitone.
E. rostrata	0.1	0.912 to 0.925	—1.1 to +13	Cineol; valeric aldehyde.
E. Staigeriana	3	0.880 to 0.901	...	Citral; terpenes.
E. Woolsiana	0.5	0.889	—13.7	Aromadendral; cineol (traces).

Geranium Oil. Rose Geranium Oil.

The true geranium oil is distilled from the fresh flowering herb of species of *Pelargonium*, chiefly varieties of *P. odoratissimum, capitatum*, and *roseum*. The plants are cultivated very largely in Algeria, though French and Réunion oils are also found in commerce. Rose-petals are not infrequently distilled with the geranium plant to obtain a finer product, so that a true geranium oil is somewhat difficult to procure. The true geranium oils should not be confused with the so-called Indian (Turkish) "geranium" oil (Palmarosa oil), a product of the leaves of *Andropogon Schœnanthus* (see p. 393), which is largely used as an adulterant of rose otto.

[1] The oil from *Backhousia citriodora* (which tree, like the *Eucalyptus citriodora*, is found in South Queensland) consists almost entirely of citral (93 to 95 per cent.). The oil does not appear to be on the market.

Geranium oil is a colourless or slightly green or brownish oil of pleasant rose-like odour. Its specific gravity ranges from 0.890 to 0.906 at 15.5° C., and its optical rotation (100 mm.) varies between the limits —6° to —16°. The oil is soluble in 3 volumes of 70 per cent. alcohol, a factor which is very useful in detecting adulteration.

The following table shows the physical characters of the different commercial varieties of geranium oil (Gildemeister and Hoffmann, *The Volatile Oils*, p. 450). The figures for the German oil are added, though this is not an article of commerce:—

VARIETY.	YIELD, PER CENT.	SPECIFIC GRAVITY.	OPTICAL ROTATION (100 MM.)	SOLUBILITY IN 70 PER CENT. ALCOHOL.	ESTERS (AS GERANYL TIGLATE). PER CENT.
French,	0.15 to 0.33	.897 to .905	—7.3 to —9	2 to 3 vols.	25 to 28
Réunion,		.889 to .895	—8 to —11	2 to 3 vols.	27 to 33
Algerian,		.892 to .900	—6.3 to —10	2 to 3 vols.	19 to 29
Spanish,		0.897	-10 to —11	Not soluble owing to presence of a paraffin.	35 to 42
German,	0.16	0.906	—16	...	28

Geraniol is the chief constituent of geranium oil, which also contains citronellol. The two alcoholic constituents of the oil vary in amount from 60 to 70 per cent. (free), and in addition 20 to 40 per cent. of their esters are present, chiefly tiglates. (Detailed information concerning the proportions of the alcoholic constituents, and their determination and separation, will be found on pp. 327, 332.) A considerable amount of free acid is sometimes present in geranium oils, while esters of caproic, and probably of acetic, butyric and valeric acids also occur in small quantities. The Algerian oils contain a smaller proportion of esters than other varieties. In addition, geranium oil contains lævo-menthone, and small amounts of pinene, phellandrene, amyl alcohol, linalol, and a paraffin melting at 63° C. Réunion oil is also stated to contain a blue high-boiling fraction, and according to Flateau and Labbé oleic acid is present as the geranyl ester, while other geranium oils are said to contain an acid having the formula, $C_{14}H_{28}O_2$.

Geranium oils are liable to adulteration with fatty oils, and with the oils of turpentine and cedar-wood. All such additions tend to decrease the solubility of the oil in 70 per cent. alcohol. Fatty oils would be further detected by the presence of a non-volatile residue. The paraffin naturally occurring in geranium oils will rise to the surface on the addition of alcohol, while fatty oils tend to fall to the bottom of the containing vessel.

Geranium oil is largely adulterated with the so-called Indian geranium oil (p. 393), an addition which causes a lowered ester-value.

Geranium oil is largely used in perfumery and is known as "rose-geranium" owing to the common practice of adding rose-petals to the plants before distillation.

Juniper Oil.

This oil is obtained by the distillation of the fruit of *Juniperus communis*. The British Pharmacopœia describes the oil as being "distilled from the full-grown unripe green fruit." It has been pointed out by Schimmel & Co. (*Report*, Oct., 1898) that the oil distilled on a commercial scale is obtained from the *ripe* fruits, and that the oil from unripe fruits is in all essential qualities inferior to the normal oil from ripe fruits.

Oil of juniper is a colourless or pale greenish-yellow oil, with the characteristic juniper odour, and a warm, aromatic, bitterish taste. The British Pharmacopœia directs that oil of juniper should have a specific gravity of 0.865 to 0.890, and be soluble, with slight turbidity, in four times its volume of 95 per cent. alcohol. The U. S. Pharmacopœia describes the oil as being soluble in 10 volumes of 90 per cent. alcohol. The solubility of the oil in alcohol is a valuble aid in testing its purity, but this solubility decreases greatly with age, a fact which should be borne in mind.

The constituents of oil of juniper include pinene; cadinene; a crystalline body; a terpene-alcohol (the so-called juniper camphor); and an ester, probably the acetic acid ester of this terpene-alcohol, boiling at 180°.

The specific gravity of juniper oil usually ranges from 0.867 to 0.875, and these limits include the majority of samples. The pharmacopœia limits are therefore wide enough to include all genuine oils, and any departure from these limits may be taken as fairly certain evidence of adulteration. Old oils become thick through slow resinification and acquire an acid reaction and a more or less rancid odour. The age of the berries from which the oil is distilled also influences the specific gravity of the oil.

Juniper oil is lævo-rotatory to the extent of about —10° in a 100 mm. tube. It rarely exceeds this limit, and is usually much less active, ranging from very slightly lævo-rotatory to about —5°. Gildemeister and Hoffmann state that the oil is sometimes faintly dextro-rotatory.

Juniper oil is largely used for the manufacture of "gin-essence" (artificial gin). The true spirit is obtained by the distillation of the fermented juniper-berries, but gin-essence is an article of

commerce consisting almost entirely of a solution of juniper-berry oil in alcohol.

Oils from the berries of *Juniperus phœnica* and of *J. oxycedrus* have a lower specific gravity than the ordinary oil of juniper (.850 to .860). Their optical activity is similar to that of the ordinary oil of juniper-berries. The *wood* of *J. oxycedrus*, on destructive distillation, yields the oil known as *Cade Oil.*

Fractional distillation serves as a method for the approximate determination of the pinene and cadinene in the oil. E. J. Parry states that with a series of fractionating-bulbs, from 25 to 35 per cent. of the genuine oil will distil between 155° and 160°, and from 10 to 20 per cent. between 270° and 280°.

The wood of *J. communis*, when distilled with steam, is said to yield a volatile oil, but it is not an article of commerce. Commercial juniper-wood oil[1] is, according to Parry, either an oil obtained by distilling turpentine oil over the wood, or more often a mixture of turpentine with the oil from the juniper-berry. Less frequently it is composed of the waste terpenes from the preparation of so-called terpeneless oil of juniper.

Lavender Oils.

The true lavender oil is obtained by the distillation of the flowers of *Lavandula vera*. It is a pale yellow or colourless oil, with a fragrant odour of the flowers, and a pungent bitter taste.

The British Pharmacopœia directs that the oil should have a specific gravity not less than 0.885, and that it should dissolve in 3 volumes of 70 per cent. alcohol. J. C. Umney is of opinion that the lower limit for the specific gravity of English lavender oil should be fixed at 0.883.[2]

The two chief varieties of this oil are the English and the French. French oil of lavender contains linalol;[3] linalyl acetate (25 to 40 per cent.); traces of pinene, limonene and a sesquiterpene; geraniol (probably as esters); cineol; a stearopt-

[1] A number of prosecutions have been instituted under the Food and Drugs Acts for the sale of "juniper oil" consisting of juniper-wood oil, and for adulteration of the oil with turpentine oil.

[2] The usual English method of distilling lavender oil consists in collecting the last runnings (4 to 8 per cent. of the total distillate) apart from the major portion, since towards the end of the distillation decomposition-products come over, causing a deterioration in the odour of the oil. The first distillates, as was shown by J. C. Umney's experiments, have a lower sp. gr. (down to 0.881 in recently distilled samples) than the last runnings, which contain a larger proportion of esters.

[3] This constituent was first discovered by Semmler and Tiemann (*Ber.*, xxv, p. 1180), who termed it *lavendol*. It remained for Bertram and Walbaum (*Jour. prakt. Chem.*, xlv, p. 590) to point out its identity with linalol.

ene; coumarin; and coumaric acid.[1] English oil differs from the French oil mainly in its percentage of linalyl acetate (7 to 9 or 10 per cent. only), and in containing a fairly large proportion of cineol, which imparts a characteristic pungency to the oil. The districts cultivating the plant in England are chiefly Surrey, Kent, and Lincolnshire.

The specific gravity of both English and French lavender oils varies between 0.885 and 0.900, rarely falling to 0.882. It increases somewhat with age. The addition of alcohol[2] or turpentine oil as an adulterant lowers the specific gravity; while admixture of spike-lavender or cedar-wood oil raises this constant. Schimmel & Co. have observed the adulteration of lavender oil with resin, the addition of which raises the specific gravity of the oil.

The optical rotation of oil of lavender is not mentioned in the British Pharmacopœia. It varies from about —4° or —5° to —10°. Lavender oils frequently suffer adulteration with oil of spike-lavender, when the optical activity is decreased, since spike oil is dextro-rotatory, + 1° to + 5°. American turpentine oil has a similar effect, while the lævo-rotation is also increased by the addition of French turpentine or cedar-wood oil.

The odour of oil of lavender is dependent on more than one of its constituents. That such is the case is shown by the fact that the English oil, containing far less linalyl acetate than French oil, can command a much higher price. Thus the determination of the ester-content of an oil is not sufficient to decide its quality, and in the case of English oils at least it is necessary to take into account the purity of the odour as well as the chemical constants of the samples. Schimmel & Co. contend that the value of the oil increases as the ester-content rises. There can be no doubt that the odour of lavender oil, due partly to the linalyl acetate (which has a bergamot odour), is modified to a very appreciable extent by other constituents probably as yet unknown. E. J. Parry is of opinion that no definite relation exists between the ester-content and the perfume-value of French oil of lavender.

The determination of the ester-content is of value when comparing oils from the flowers grown in the same district. The

[1] M. Duyk (*Jour. Pharm. Chim.*, 1896, p. 453) states that lavender oil contains, in addition to the compounds mentioned in the text, borneol, and its acetic, butyric, and valeric esters. Bouchardat (*Bull. Soc. Chim.*, 1894, p. 147) found dextro-camphene in the oil. Schimmel & Co. (*Reports*, April and October, 1903) have announced the discovery of ethyl-amyl ketone, $C_8H_{16}O$, furfural (in first fractions), iso-amyl alcohol and an isomeric alcohol, together with esters of the former, in French lavender oil.

[2] "When the oil is shaken with water in a narrow graduated cylinder, its volume should not be diminished (absence of alcohol)."—*U. S. Pharmacopœia* (8th Rev.).

method usually employed is described on p. 231. English oils usually contain from 7 to 10 (sometimes 12) per cent. of esters (calculated as linalyl acetate), while French oils contain about 30 to 40 per cent. or more. The finest oils produced in the south of Europe are those distilled from plants grown at great elevations.

The amount of esters present in oil of lavender is lowered by adulteration with either turpentine or spike-lavender oil, neither of which contains any notable amount of esters. Thus, as pointed out by E. J. Parry, mixtures of French lavender oil and spike oil can be made, having the same ester-content (about 10 per cent.) as English oil, but the optical rotation will be lowered and the specific gravity raised, though not to a very great extent. Much lavender oil is now adulterated with spike oil *and* ethyl succinate (see below).

Other less important varieties of lavender oil are described in the table on p. 504.

The presence of much cineol in the oil may be taken as evidence of the presence of spike oil so far as French oil of lavender is concerned, but English oil of lavender contains naturally notable amounts of cineol.

Schimmel & Co. have called attention to the adulteration of lavender oil with ethyl succinate, evidently added to give a fictitious ester-value to the oil. Two samples adulterated with this substance had a high specific gravity (0.900; 0.905), and a high ester-value, (47.5; 48.5 per cent.).[1] For the detection of such adulteration, Schimmel & Co. proceed as follows: About 2 grammes of the oil is saponified, and the portion insoluble in water washed out with ether, the aqueous residue neutralised with acid, and diluted up to 50 cc.; 10 cc. of cold saturated barium chloride solution is added, the liquid warmed on the water-bath for two hours, and then cooled. The formation of any crystalline precipitate is indicative of adulteration, since the barium salts of acetic and butyric acids (the normal organic acids of lavender oil) are soluble.

Salicylic and benzoic acids have also been added to lavender oil. Their presence is easily detected by the determination of the acid-number. Pure oil of lavender is practically free from acidity.

Spike Lavender Oil.

This oil is obtained by the distillation of the flowering herb, *Lavandula spica*. It is a pale yellow oil, with an odour resembling at the same time lavender and rosemary oils.

[1] These adulterated oils contained approximately 8 per cent. of ethyl succinate, which would require about the same amount of potash for saponification as 18 per cent. of linalyl acetate.

Whereas true lavender oil contains a notable amount of esters, oil of spike lavender is practically free from them, but contains a considerable proportion of alcoholic constituents. The composition of spike oil, which has been worked out chiefly by Bouchardat (*Compt. rend.*, cvi, p. 551; cvii, p. 53), is as follows:—Linalol; cineol (a larger amount than English lavender oil); *d*-pinene; *d*-camphene; camphor; borneol; terpineol; and geraniol. A sesquiterpene is also supposed to be present, and traces of esters of the various alcohols also occur in the oil. The alcoholic bodies, as determined by the acetylation process and calculated as linalol, usually constitute about 30 to 40 per cent. of the oil. The method for the determination of the alcohols in essential oils is given on page 229. The results are not strictly accurate, on account of the ease with which the alcohols decompose, but valuable comparative results are obtainable.

The specific gravity of spike lavender oil varies from 0.904 or 0.905 to nearly 0.920, but it rarely exceeds 0.915. Probably 0.918 should be taken as the maximum limit. Adulteration with turpentine oil lowers the specific gravity.

The optical rotation of spike oil varies from —3° to +4°, rarely up to +7°. Oils exceeding a rotation of +5° should be regarded with suspicion.

Schimmel & Co. have proposed to fractionate the oil and take the optical rotation of the first 10 per cent. distilled. All spike oils of undoubted purity are stated to give a distinct dextrorotatory fraction,[1] whilst any appreciable amount of French turpentine oil added to spike oil will render the fraction lævorotatory. It is necessary, in carrying out this test, to use Ladenburg's flasks of uniform size, and to distil the fraction (5 cc. from 50 cc. of the oil) at the rate of not more than one drop per second. The following results were obtained by Schimmel & Co. by the analysis of four samples of genuine spike oil:—

Number.	Specific Gravity.	Rotation ° in 100 mm. Tube.	Solubility in 70% Alcohol.	Rotation ° of First 10 per cent. of Distillate. (100 mm.)
1............	0.915	+7.1	1 in 3	+7.2
2............	0.915	+7.0	1 in 2	+5.2
3............	0.914	+5.0	1 in 2½	+7.2
4............	0.918	+5.5	1 in 2½	+6.1

Parry and Bennett lay stress on the importance of examining the various fractions obtained by the distillation of spike oil. An

[1] Parry and Bennett have shown that certain spike oils are not only lævo-rotatory, but may yield a lævo-rotatory first fraction on distillation. A determination of the total alcohols is required in these cases to ensure absence of French turpentine oil.

adulterated oil examined by them gave a fraction at 230° to 240° C. consisting of safrol.

Spike oil is soluble in three volumes of 70 per cent. alcohol. In this form, however, the solubility of spike oil is not of much value as a test for adulteration, since it has been shown by Parry and Bennett (*Chem. and Druggist*, 1903, p. 1011) that 25 per cent. of certain cheap adulterants may be added to spike oil without altering the solubility in 70 per cent. alcohol or the physical characters of the oil. Parry and Bennett suggest therefore that the solubility test should be altered, since it has been found that pure spike oils are soluble in six volumes of 65 per cent. alcohol. An addition of 5 to 10 per cent. of the usual adulterants (common rosemary oil, turpentine oil and safrol) disturb this solubility.

Genuine spike oils yield practically no ester-value. This figure, together with the specific gravity, optical rotation, rotation of the first 10 per cent. distilled, and determination of the free alcohols, are most valuable data for testing the purity of this oil.

Lemon Oil.

This oil is produced chiefly in Sicily and the Riviera, and is probably one of the most complex of the essential oils. It is obtained by expression of the fresh peel of lemons (*Citrus medica*).

Lemon oil contains dextro- and lævo-limonenes; citral (geranial); citronellal (?);[1] geraniol; terpineol; geranyl and linalyl acetates; and a crystalline stearoptene (citraptene, consisting chiefly of *limettin* or dimethoxy-coumarin, $C_{11}H_{10}O_4$) melting at 145° C. Lævo-pinene, phellandrene, camphene, methyl anthranilate (Parry), methyl-heptenone and a resin also occur normally in small quantities, while Burgess and Child have recently shown that octyl and nonyl aldehydes (and possibly decyl aldehyde) are also present.[2]

Limonene is the constituent of lemon oil which occurs in the greatest proportion. The compound to which the odour and strength of the oil is chiefly due, however, is citral.[3] The characters of this aldehyde and of citronellal, and the methods for

[1] H. E. Burgess states that it is doubtful if genuine oils ever contain citronellal.

[2] According to Schimmel & Co., lemon oil also contains a sesquiterpene which is probably lævo-rotatory.

[3] While citral is responsible for the primary odour of lemon oil, the esters geranyl acetate (in Messina and Palermo oils) and linalyl acetate (in Palermo oils), together with small amounts of octyl and nonyl aldehydes and other bodies, modify it to such an extent that the purest citral obtainable is but a poor substitute for a lemon flavour.

their determination, are described on pages 335, 338. There has been much controversy as to the normal amount of citral (or rather, of total aldehydes) present in genuine oil of lemon, a standard of 7 per cent. being until recently insisted on. It is now acknowledged, at least by most English chemists, that the citral-content of pure lemon oil rarely, if ever, exceeds 4 per cent., and is usually lower (3 per cent.). This conclusion is based mainly upon the well-known fact that the yield of terpeneless oil of lemon is only 5 to 6 per cent. of the original oil, while the concentrated product contains about half its weight of citral. A standard of not less than 4 per cent. citral has been adopted in the U. S. Pharmacopœia, the oil being assayed by a given method.[1] Lemon oil containing an addition of lemongrass oil or lemongrass citral would of course give a higher aldehyde content.

Umney and Swinton (*Pharm. Jour.*, 1898, p. 196) have found geranyl acetate to be present in lemon oil to the extent of 1.2 to 1.4 per cent. This is true both of the Messina and Palermo varieties of the oil, but in the latter a small quantity of linalyl acetate is also present.

Lemon oil has probably suffered more from adulteration than any other essential oil. The adulterants include oil of turpentine, lemon and orange terpenes, distilled orange and lemon oils, lemongrass oil, lemongrass citral, cedar-wood oil, alcohol, stearin, &c.

The British Pharmacopœia states that lemon oil should have a specific gravity of 0.857 to 0.860, and an optical rotation of not less than $+59°$ for 100 mm. It is further directed that the optical rotation of the first 10 per cent. distilled should not differ by more than 2° from the original oil. The last requirement is based on error, and is met by very few pure oils.[2]

[1] This method, which is substantially that of S. P. Sadtler (*Amer. J. Pharm.*, 1904, lxxvi, 84), is directed by the U. S. Pharmacopœia (8th Rev.) to be carried out as follows:—Weigh accurately about 15 cc. of lemon oil into a 150 cc. flask, add 5 cc. of distilled water and a little phenolphthaleïn solution, and exactly neutralise the liquid by the addition of decinormal sodium hydroxide. Add next 25 cc. of a neutral solution of sodium sulphite (1 in 5), and immerse the flask in a boiling water-bath. Run in from a burette as required, with frequent shaking, sufficient half-normal hydrochloric acid to keep the hot liquid neutral. When the liquid remains permanently neutral, note the cc. of half-normal acid added. A blank test must be carried out simultaneously. The number of cc. of half-normal acid obtained by subtracting the volume required by the blank experiment, from the cc. of acid used in the determination, multiplied by 0.03802×100, and divided by the grammes of sample taken for the analysis, gives the percentage of citral in the lemon oil. The method gives useful comparative, if not strictly accurate, results.

[2] The U. S. Pharmacopœia (8th Rev.) requires lemon oil to have an optical rotation of not less than $+60°$ at 25° C. The error in the rotation of the first ten per cent. distilled, given by the British Pharmacopœia, is repeated in the U. S. Pharmacopœia.

The specific gravity of genuine lemon oils varies between the limits 0.856 to 0.862 or 0.863. These figures are but little altered by admixture with turpentine oil or with turpentine and orange oils, but any addition of alcohol will disturb the specific gravity and may thus be readily detected. Oils of specific gravity 0.853, such as have recently been met with, were very possibly adulterated with a small quantity of lemon terpenes.

The optical rotations of lemon oil and its fractions obtained by distillation are probably the most valuable figures for determining the purity of the oil. Pure lemon oils rarely have an optical rotation outside the limits +58° to +66°,[1] the great majority of oils coming within the narrower limits +59° to +64° at 20° C. (for 100 mm.). The figures vary slightly in different years. The average rotation of Palermo oils is a little lower than that of Messina oils. Schimmel & Co. recommend the distillation of 50 cc. of the oil in a fractionating apparatus, the first 10 per cent. distilled (5 cc.) being examined in the polarimeter. This fraction should have an optical rotation lower by not more than 5° than that of the original oil (S. & Co.).[2] The refractive index of the fractions of lemon oil may yield useful information, but the method possesses no advantages over a polarimetric examination.

About 20 to 30 per cent. of lemon oil distils between 172° and 174° C.

The addition of oil of turpentine to lemon oil causes a decrease in rotatory power, but if an admixture of orange terpenes together with turpentine oil has been made, the rotation of the original oil may not be affected. Careful fractional distillation can alone give definite information with respect to these additions. The apparatus employed should be used also for the distillation of some authentic samples of lemon oil, in order to obtain standard results for comparison. Genuine lemon oil always shows a large increase in optical rotation of the later fractions over the first 10 per cent. distilled. The following table, by Burgess and Child (*J. S. C. I.*, 1901, xx, p. 1176) gives the constants and behaviour on fractional distillation of five samples of genuine oil of lemon. One hundred cc. of oil was distilled in each case:—

[1] According to Burgess and Child (*J. S. C. I.*, 1901, p. 1176), certain lemon oils at the earlier part of the season may have a rotation of +68° for 100 mm., but such oils are not usually met with in the market, and are mixed with lemon oil of a lower activity.

[2] The addition of a small quantity of turpentine oil (5 per cent.) has very little influence on the optical rotation of the first 10 per cent. of the distillate, since the oil of turpentine does not come over to any great extent at this stage. E. J. Parry is of opinion that the examination of the rotation of the successive fractions (in 20 per cent. quantities) will yield valuable information, but the subject requires further investigation.

CONSTANTS OF PURE LEMON OIL (Burgess and Child).

	Particulars of Oils.	Physical Constants of Original Oils.	Distillation.			Citral Content of Third Fraction.
			No. of c.c.	Rotation in 100 mm. Tube.	Zeiss Readings. 20° C.	
I.	Genuine Oil of good quality. (Messina.)	Sp. Gr. = 0.857 Rotation = +63° 12′ Ref. Index = 1.4755	10 80 7.5	+55° 30′ +70° 40′ +10° 56′	72.0 72.4 82.5	42%
II.	Genuine Oil (Palermo). Not typical.	Sp. Gr. = 0.857 Rotation = +61° 27′ Ref. Index = 1.4757	10 80 7.5	+54° 6′ +67° 45′ +19° 13′	72.2 72.4 81.5	35%
III.	Genuine Oil of very high gravity.	Sp. Gr. = 0.862 Rotation = +58° 30′ Ref. Index = 1.4771	10 80 7.0	+50° 41′ +67° 16′ — 6° 0′	72.0 72.7 90.6	64%
IV.	Genuine Oil of high gravity.	Sp. Gr. = 0.860 Rotation = +60° 36′ Ref. Index = 1.4769	10 80 7.0	+50° 6′ +68° 43′ — 3° 20′	72.2 72.6 88.6	64%
V.	Genuine Oil, new crop, 1901.	Sp. Gr. = 0.858 Rotation = +61° 28′ Ref. Index = 1.4754	10 80 7.0	+51° 47′ +69° 2′ + 8° 14′	71.8 72.3 81.9	40%

The adulteration of lemon oil with orange or lemon terpenes (without addition of turpentine oil) may be inferred from the lowered specific gravity, slightly increased rotation, and in the increase of non-aldehydic constituents. Oils adulterated in this manner have, however, frequently also received an addition of lemongrass citral. If the oil be distilled *in vacuo*, and the odour of the terpeneless portion observed, the addition of lemongrass oil or lemongrass citral will be detected. The optical rotation of this residue may also yield some information. A determination of the non-volatile matter and of the saponification-number of lemon oil will serve for the detection and determination of added fatty substances.

Lemon oil rapidly deteriorates on keeping. It is best stored in tightly-stoppered bottles filled up to the neck and kept in a cool, dark place. The turbidity of certain specimens of lemon oil is usually due to the presence of a small quantity of water.

Methods for the examination of *lemon flavouring extracts* (essences) and their substitutes have been published by A. S. Mitchell (*J. A. C. S.*, 1899, xxi, 1132; abst. *J. S. C. I.*, 1900, p. 179); and by Wender and Gregor (abst. *J. S. C. I.*, 1900, p. 372).

Nutmeg Oil.

This oil is obtained by the distillation of the nutmeg, the fruit of *Myristica fragrans*. It is a colourless or pale yellow oil, having the odour and taste of nutmeg. It absorbs oxygen and becomes darker and thicker on exposure to the air.

The British Pharmacopœia (1898) directs that oil of nutmeg should have a specific gravity of 0.870 to 0.910. It should form a clear solution with its own volume of 95 per cent. alcohol, and a little of the oil evaporated on a water-bath should not leave a residue which crystallises on cooling. This ensures the absence of the concrete oil of nutmeg, which may occasionally be carried over in the distillation.[1]

The limits of specific gravity for this oil, as laid down by the British Pharmacopœia, are regarded by various observers as being too narrow. Schimmel & Co. give the gravity of oil of nutmeg as 0.865 to 0.920, while E. J. Parry considers that the limits of 0.868 to 0.915 are not too wide.

Oil of nutmeg is dextro-rotatory, the limits being from +14° to +28° or 30° in a 100 mm. tube.

[1] E. J. Parry has pointed out that the presence (even in traces) of the fixed oil of nutmeg is said to be objectionable in oil of nutmeg used for the manufacture of *sal volatile*. The residue on evaporation of the oil, after purification with alcohol, consists chiefly of *myristic acid*, melting at 54° C.

The composition of oil of nutmeg is not yet known with certainty, and the subject needs further investigation. The oil contains a large amount of terpenes, including dextro- and lævo-pinenes and dipentene. The presence of *myristicol* has been noticed by Gladstone and by Wright. The former observer states that this substance has the formula $C_{10}H_{14}O$, and a boiling point of 224° C. According to Wright, however, its formula is $C_{10}H_{16}O$, and its boiling point 212° C.

Myristic acid appears to be present to a small extent in the oil passing over towards the end of the distillation. It separates out on standing. Thus oil of nutmeg which conforms to the B. P. limits is really a fractionated oil, that passing over towards the end of the distillation being rejected for pharmacopœial uses. The highest boiling fractions of the oil appear to contain small quantities of a phenol.

Mace Oil.

This oil is very similar to oil of nutmeg, and indeed the commercial product is frequently nothing else than nutmeg oil distilled from nutmegs of inferior quality.

Genuine oil of mace is the product of distillation of the arillode of the seed of *Myristica fragrans*. The true oil of mace is a colourless, yellowish, or dull-red oil, having a specific gravity of 0.910 to 0.930 (or, according to Gildemeister and Hoffmann, 0.890 to 0.930). The optical rotation of the oil is about +10°, or even up to +20°. Oil of mace is completely soluble in three parts of 90 per cent. alcohol.

The composition of oil of mace is very similar to, if not actually identical with, that of oil of nutmeg. Generally speaking, oil of nutmeg appears, however, to contain more terpenes than oil of mace. F. W Semmler (*Berichte*, 1890, p. 1805) found in the higher boiling fractions, a crystalline compound forming white needles, melting at 30°. This substance has, according to the most recent work of Semmler and H. Thoms, the formula $C_{11}H_{12}O_3$, and was named by Semmler *myristicin*. It appears to be *methoxy-dioxymethylene-allyl-benzene*, $C_6H_2.(C_3H_5).(OCH_3)(O.O.CH_2)$.

The oils of nutmeg and mace are so similar that they are frequently sold indiscriminately, and it is therefore practically impossible to obtain authentic samples of true nutmeg or true mace oil.

Orange Oils. OILS OF BITTER AND SWEET ORANGE-PEEL.

The oils of bitter and sweet oranges are obtained by expression from the fresh peel of the fruits of *Citrus bigaradia* and *C.*

aurantium respectively, and are very similar in physical properties and composition. The oil produced from orange-flowers is known as "neroli oil" (page 443).

Sweet orange oil is an orange-yellow oil with the characteristic orange odour and an aromatic taste. It consists largely (90 per cent.) of dextro-limonene (Wallach). The oil contains in addition the following bodies, most of which are present in mere traces or in very small amonnts: lævo-limonene; pinene (?); citral; citronellal;[1] linalyl acetate; *d*-linalol (Parry); nonylic alcohol; decylic alcohol; *d*-terpineol; normal decylic aldehyde; esters of butyric acid and of its immediately higher homologues (Parry); an ester of caprylic acid; methyl anthranilate or ortho-amido-benzoate (Parry[2]); and, according to Flatau and Labbé (*Bull. Soc. Chim.* [3], xix, 361) another aldehyde (of unknown composition), myristicol, and myristinic acid.[3] These observers also isolated from sweet orange oil an ester (the acid of which contains 21 atoms of carbon[4]) in the form of an insoluble amorphous powder, melting at 64° to 65°. This compound had a strong odour of oranges.

Bitter orange oil is a yellow liquid with a bitter aromatic taste, and a delicate orange odour. It contains limonene, citral, and linalyl acetate. These are the only constituents that have as yet been recognised with certainty.

The specific gravity of sweet orange oil ranges from about 0.848 to 0.852; that of bitter orange oil from about 0.853 to 0.854 at 15°. The specific gravity is not much altered by adulteration with oil of turpentine, but the addition of alcohol makes a considerable change. The following physical characters of the oils have been recorded by Schimmel & Co. and Bush & Co.:—

	Sweet Orange Oil.		Bitter Orange Oil.	
	S. & Co.	B. & Co.	S. & Co.	B. & Co.
Specific gravity at 15° C....	0.848 to 0.852	0.8495 to 0.8510	...	0.853 to 0.854
Optical rotation[5] at 20° for 100 mm..............	+96° to +98°	+96° to +99°	+92° to +98°	+91° to +94°

[1] K. Stephan denies that orange oil contains either citral or citronellal.

[2] This substance was found by E. and H. Erdmann and Schimmel & Co. to be present in oil of neroli. It is an oily body having an odour resembling neroli oil. In solution it possesses a fine characteristic fluorescence.

[3] K. Stephan has isolated an acid similar to or identical with cerotic acid.

[4] E. J. Parry has isolated this acid, and from an analysis of the silver salt finds that it cannot have a greater molecular weight, if it is monobasic, than 275. This allows only 17 atoms of carbon to the molecule.

[5] The optical rotation of orange oils varies more with the temperature

Orange oils have a higher optical rotation than any other essential oil. Any adulteration must therefore cause a lowering in this constant. The greatest change in the optical rotation of orange oil is produced by turpentine oil. Lemon oil also lowers the rotatory power, but to a smaller extent. An addition of lemon or turpentine oil to orange oil raises the specific gravity.

In order to detect the presence of turpentine oil in orange oils, a fairly large quantity of the sample should be subjected to repeated fractional distillation, using a dephlegmator. The pinene will be contained in the first fractions, and may be recognised by its boiling-point and optical rotation. (This will be lævo- or dextro-rotatory according as the adulterant is French or American turpentine oil.) In the case of a genuine sample of orange oil, the first distillate will show a slightly higher optical rotation than the original oil. (First 10 per cent. should be *at least* 1° higher in optical rotation.) An adulterated sample (containing lemon oil or its terpenes, &c.) will give a distillate having a lower rotation than the original oil. If the evidence obtained is not satisfactory, the pinene-nitrosochloride compound should be prepared, and from this pinene-nitrolbenzylamine, or pinene-nitrol-piperidine, may be obtained. The presence of large amounts of oil of turpentine may frequently be detected by simply observing the original optical rotation of the oil.

Oil of sweet orange-peel is official in the U. S. Pharmacopœia, which directs that it should have an optical rotation of not less than +95° and that the first fractions distilled should give no evidence of the presence of pinene as determined by the isolation of the nitroso-chloride (absence of turpentine oil).

Pure orange oil begins to boil at about 173° to 174°. J. C. Umney found that the pure oil, on fractional distillation, gave 20 per cent. of distillate between 173° and 175°; 61 per cent. between 175° and 178°; 14 per cent. between 178° and 188°; leaving 5 per cent. of residue. Admixture with much oil of turpentine will lower the boiling-point of the oil.

DISTILLED ORANGE OIL,[1] and the residual products from the

than in the case of lemon oil. When the rotatory power has been observed at temperatures below 20° C., 0.24° must be subtracted for each degree below this temperature; whilst for temperatures above 20° C. 0.22° must be added for each degree to obtain the angle of rotation for the standard temperature.

[1] Distilled orange oil is inferior to the expressed oils, owing to the deterioration consequent upon the distillation process, which injures the oxygenated constituents. Schimmel & Co. give the following figures obtained by the examination of two distilled oils of orange:—

	BITTER.	SWEET.
Specific gravity,	0.853	0.855
Optical rotation (100 mm.),	+96.97°	+95.95°

manufacture of terpeneless oil of orange, are occasionally used as adulterants of orange oil. When present in any considerable quantity, both these additions render the colour of the oil very pale, they lower the specific gravity, and have a deleterious effect upon the odour of the sample. The terpenes of lemon oil are also used as adulterants and have a similar effect.

Oil of orange is acted upon by light and air in the same manner as lemon oil (page 435).

The concentrated or terpeneless oil of sweet orange is a somewhat complex oil having a specific gravity of about 0.900 and an optical rotation of about +10°. At a pressure of 10 mm. terpeneless oil of orange distils between 100° and 150° C. E. J. Parry found terpeneless oil of orange-pea (immature fruit) to have a specific gravity of 0.910 and an optical rotation of +6.5°.

E. J. Parry has examined a sample of the essential oil obtained from the peel of the immature fruit of the orange, *i. e.*, when about the size of a pea (orange-pea oil). The oil is interesting, since it forms a connecting link between neroli oil and the fruit oil. The pea oil was found to contain dextro- and lævo-limonene, dextro-linalol, and terpineol, and also a trace of methyl anthranilate, but such a small trace of this compound was present that it is clear almost all had disappeared in the early stage of fructification. The following comparison of the characters of the oil with neroli oil and the fruit oil is instructive. The decrease in specific gravity and increase in optical rotation show the gradual increase in the proportion of terpene present:—

	Sp. Gravity.	Optical Rotation.
Neroli,	0.870 to 0.880	+4° to +15°.
Orange-pea,	0.862	+71.25°.
Orange,	0.850	+96°.

Tangerine orange oil was found by E. J. Parry to differ somewhat in properties from the ordinary orange oils. It is probably identical with the oil of Mandarin orange. The following table shows the physical characters and composition of the oils:—

	Tangerine Orange Oil.	Mandarin Orange Oil.
Source,	....	Expressed peel of *C. madurensis*.
Appearance,	....	Golden-yellow, with slight bluish fluorescence.
Specific gravity,	0.8589	0.854 to 0.858
Optical rotation, °,	+70.8	+67 to +73
Boiling-point, ° C.,	....	171° to 175°
Constituents,	A camphoroid (limettin ?).	Chiefly dextro-limonene; traces of dipentene, citral (1%) and citronellal; methyl ester of methyl anthranilate; decyl and nonyl aldehydes; linalol; terpineol.

On cooling tangerine oil to a low temperature, fine yellow needle-shaped crystals separate out. They retain their colour after recrystallisation from alcohol, and melt at 70° C. Parry has suggested that this substance is identical with the "*limettin*" from limette oil, or at least contains that compound.

According to E. J. Parry, mandarin orange oil contains, in addition to the bodies given in the foregoing table, about 1 per cent. of the ester found in ordinary orange oil by Flatau and Labbé (p. 437). The blue fluorescence of the oil is stated to be due to the presence of the methyl ester of methyl-anthranilic acid, $C_6H_4(NH.CH_3).COOCH_3$. A valuable paper by Bertè and Gulli on the detection of the adulterants of Mandarin orange oil by the observation of the optical rotation before and after distillation will be found in the *Chem. and Druggist*, 1905, p. 445.

Hesse and Zeitschel (*Ber.*, 1901, xxxv, 296; abst. *J. S. C. I.*, 1901, pp. 289; 1138) have proposed the following method for the detection and determination of methyl anthranilate in essential oils, based upon the precipitation of the ester with sulphuric acid, and the subsequent saponification of the ester. The oil to be examined is dissolved in two to three parts of dry ether, the solution cooled at least to 0° C., and a cold mixture of 1 measure of strong sulphuric acid with 5 measures of ether is added, drop by drop, with continual stirring, until no further precipitate forms. The precipitate and any other insoluble matter is brought into solution by means of alcohol, and the liquid titrated with semi-normal alkali, phenolphthaleïn being the indicator. The solution is then saponified by boiling with excess of alcoholic potash for 30 minutes. The quantity of methyl anthranilate may be calculated from the acid value of the ester sulphate.[1] If the precipitate contains principally the sulphate of methyl anthranilate or analogous compounds, the amounts of potash used in the two operations will be as 2 : 1. If less potash be required in the saponification than is given by this ratio, unsaponifiable bases are indicated. These may be extracted by ether from the alkaline solution. The anthranilic acid is isolated by evaporating the liquid, acidifying with acetic acid, and extracting with ether. It may be identified (and its purity confirmed) by determining the melting point alone, and also after grinding with pure anthranilic acid.

If a large quantity of the sulphate precipitate is obtained it may be dissolved as above, and an aliquot part of the solution taken for the titration and saponification. A few drops of sulphuric acid are added to the main portion of the aqueous solution, which is then shaken once with petroleum-ether to remove resins. Sodium carbonate solution is added,

[1] It is unsafe to weigh the ester-sulphate owing to its ready dissociation.

the precipitate dissolved in ether and the methyl anthranilate hydrochloride precipitated by passing a current of dry hydrochloric acid gas through the solution. The hydrochloride is purified by solution in methyl alcohol and precipitation by ether. Other bases forming soluble hydrochlorides will be found in the ethereal solution. The ethereal liquid from the original sulphate precipitate is washed with water to remove excess of sulphuric acid, and the ether removed. The liquid may then be used for the detection and determination of other constituents present in the oil, which will remain unaffected in the above process.

The following method for the detection and determination of methyl anthranilate is due to E. Erdmann (*Ber.*, 1902, xxxv, 24; abst. *J. S. C. I.*, 1902, p. 283). The process depends upon the formation of an azo-dye when methyl anthranilate, the only primary base as yet known to occur in essential oils, is diazotised in the presence of an aromatic phenol, such as β-naphthol. When only very small quantities of the ester are present, a colorimetric modification of the method is employed, a sufficient amount of an aqueous solution of β-naphthol-disulphonic acid R being added to the solution of the ester after diazotisation, and the tint obtained compared with a standard solution of methyl anthranilate when quantitative results are required. In the case of larger amounts of the ester, Erdmann prefers to dilute the diazotised solution of the ester (obtained by treating its hydrochloric acid solution with sodium nitrite for ten minutes) to a known volume, and then titrate with it 10 c.c. of a 0.5 per cent. alcoholic solution of β-naphthol (rendered alkaline with caustic soda), the end-reaction being observed by "spot" tests, or by filtering a small portion of the liquid and testing it with the diazo-compound and with the naphthol solution. The insoluble orange-coloured dye[1] produced falls to the bottom of the vessel, and the titration is finished when no diazo reaction is obtained either by the addition of a few drops of the diazo solution or of the β-naphthol solution to a little of the filtrate from the titrated liquid. A few milligrammes of methyl anthranilate may thus be determined, and the presence of the corresponding compound of methyl-anthranilic acid does not interfere (see *J. S. C. I.*, 1900, p. 848).

The detection of methyl anthranilate by producing a *quinazoline* derivative has been described by P. Freundler (*Bull. Soc. Chim.* [3], xxxi, 882).

A *South American orange oil* has been examined by Umney and Bennett (*Brit. and Col. Druggist*, 1904, p. 169), who found it to more closely resemble orange-leaf than orange-flower oil. The odour was very pleasant, and suggested a superior

[1] This colouring matter dissolves in strong sulphuric acid with a reddish-violet colour.

petitgrain oil. As examined by Umney and Bennett, South American orange oil has a specific gravity of 0.887, an optical rotation of +2° for 100 mm., and contains 67 per cent. of total alcohols (as geraniol), of which 38 per cent. are free and 35.5 per cent. exist as esters (linalyl acetate). The oil contains lævo-pinene, dipentene, furfural, geranyl acetate, linalol and geraniol, terpineol (?) and traces of methyl anthranilate. On fractional distillation at ordinary pressure, 75 per cent. of the oil distils between 190° and 220° C. The oil is readily soluble in 2 volumes of 70 per cent. alcohol. For soap and other perfumery purposes, this oil compares favourably with French petitgrain oil.

Petitgrain Oil.

Petitgrain oil is derived from the leaves, twigs, and usually also the immature fruit of the bitter orange (*Citrus bigaradia*) by distillation with water.[1] A large proportion of the oil now comes from Paraguay.

Petitgrain oil is a yellowish oil with an aromatic and slightly bitter taste, and an odour similar to that of neroli oil, though far less delicate than the latter. Petitgrain oil is completely soluble in 2 volumes of 80 per cent. alcohol, and usually in 3 to 4 volumes of 70 per cent.

The specific gravity of petitgrain oil usually ranges from 0.885 to 0.900, though some samples may fall to 0.882. French oils have generally a lævo-rotation, but those from Paraguay are mostly dextro-rotatory. The limits are about −1° to +4° or +5°. The oil has a saponification-number of 110 to 245, equivalent to 38 to 85 per cent. of ester calculated as linalyl acetate.

Petitgrain oil as usually met with (*i. e.*, derived from the leaves, twigs and immature fruit) contains lævo-pinene (?); *l*-camphene (?); dipentene; *d*-limonene; furfural; *l*-linalol (25 to 35 per cent.); nerol; geraniol; *d*-terpineol (m. pt. 35° C.); linalyl acetate (50 to 75 per cent.); geranyl acetate; neryl acetate; methyl anthranilate (small amount); a sesquiterpene, and a pyrrol derivative. Oils which have been obtained from

[1] An oil known as "petitgrain citronnier" is obtained from the twigs, leaves, and unripe fruit of the lemon tree (*Citrus medica*). The oil has an odour similar to that of petitgrain oil, but reminding of lemon. Petitgrain citronnier has a specific gravity of 0.868 to 0.874 or higher, an optical rotation of +13° to +34°, and a saponification-number of 14.5 to 32.2. It contains citral and linalyl acetate.

"Petitgrain mandarin" is obtained similarly from *Citrus madurensis*. The oil has an optical rotation of +6.25° and contains about 45 per cent. of esters, calculated as linalyl acetate.

the leaves and twigs (only) of the plant contain little or no limonene. Petitgrain oil obtained only from the leaves of the tree contains 70 to 75 per cent of linalol, 10 to 15 per cent. of geraniol and a small proportion of a sesquiterpene.

Orange-flower Oil. NEROLI OIL.

This oil is obtained by the distillation of the flowers of the bitter orange, *Citrus bigaradia*, with water.[1] It is really the oil which separates directly from the water in the distillate (without cohobation), and is a bye-product in the manufacture of orange-blossom water, which latter is official in the British and United States Pharmacopœias.

Neroli oil is a yellowish, slightly fluorescent oil, having a powerful and very pleasant odour of orange-blossoms, and a bitter aromatic taste. It becomes brownish-red in colour on exposure to light for some time. When strongly cooled, the oil becomes turbid owing to the separation of a stearoptene, termed by Boulay in 1828 "neroli camphor." It is an odourless and tasteless paraffin (C_{27}) melting at 55° C.

Neroli oil has a specific gravity ranging from 0.870 to 0.880 (usually 0.870 to 0.875), and is slightly dextro-rotatory, about +1.5° to +5.0°, or slightly higher. The oil is soluble in 1½ to 2 volumes of 80 per cent. alcohol, the resulting solution having a violet-blue fluorescence (due to methyl anthranilate). The addition of more alcohol to this solution causes a turbidity, and crystalline flakes of the paraffin separate out. The physical properties of neroli oil, together with a comparison of the odour with oils of known origin, are valuable data in judging of its purity.[2]

The constituents of neroli oil comprise limonene; lævo-pinene;

[1] An interesting and important series of papers on the methods of manufacture of neroli oil and on the chemistry of the oils obtained by the various processes has been published by Hesse and Zeitschel (*J. S. C. I.*, 1901, 1138; 1903, 162).

[2] An oil produced by the simple distillation of the flowers of *Citrus aurantium*, sometimes termed "*sweet neroli oil*" or *Portuguese neroli oil*, is occasionally met with, though the commercial specimens of the oil sold under these names are usually derived from a mixture of various aurantiaceous oils. A sample of the true "sweet neroli oil" distilled in Germany had a specific gravity of 0.893 and an optical rotation of +16.1°. It is a dark yellow oil having an odour altogether unlike the true neroli and orange oils.

Commercial oil of sweet orange-flowers has a specific gravity of 0.860 at 23°, and an optical rotation of about +30° at the same temperature. One sample contained 6.35 per cent. of esters (as linalyl acetate), and no methyl anthranilate could be detected. According to E. Theulier, the oil contains, in addition to esters, dextro-camphene, dextro-limonene, dextro-linalol, and a paraffin

l-camphene (?); dipentene; decyl aldehyde (?); lævo-linalol (20 to 25 per cent.); geraniol; nerol;[1] phenyl-ethyl alcohol (?); dextro-terpineol (m. pt. 35° C.); *d*-nerolidol[1] (6 per cent.); linalyl, geranyl and neryl acetates (7 to 18 per cent.); esters of phenyl-acetic acid; benzoic, acetic, and palmitic acids (traces); *methyl anthranilate* (0.7 *per cent.*); *indol*,[2] *and a paraffin*. The odour of the oil and its characteristic fluorescence are largely due to the presence of methyl anthranilate.[3]

The adulterants most usually found in neroli oil are the oils of bergamot and petitgrain. Since linalol and linalyl acetate are characteristic constituents of all three oils, the detection of the two last-named in neroli oil is rendered somewhat difficult. Oil of bergamot, however, usually contains from 35 to 45 per cent. of esters, with a corresponding saponification-number of 100 to 130, while petitgrain oil contains 35 to 85 per cent. of esters, with a corresponding saponification-number of 110 to 245. *Genuine neroli oil shows a saponification-number varying* between the extreme limits of 20 and 52, corresponding to 7 to 18 per cent. of esters, but good oils usually have saponification-numbers lying between 35 and 45, equivalent to 12 to 15 per cent. of esters (as linalyl acetate). Thus an oil having a saponification-number exceeding 55 should be regarded as of suspicious character. The acetyl-number of neroli oil is about 160, equivalent to 35 to 38 per cent. of free alcohols.

It is probable that an appreciable saponification of the esters of neroli oil (to the extent of 5 or 6 per cent.) takes place during distillation, as is known to occur in lavender oil distillation (see Jeancard and Satie, *Bull. Soc. Chim.*, 1900, xxiii, 605).

Distilled oil of orange, distilled over orange-blossoms, is also fairly frequently met with as an adulterant of neroli oil.

The proportion of stearoptene present in neroli oil depends upon the extent to which the distillation of the blossoms is carried, the later fractions of the distillate containing most of

[1] Nerol and nerolidol are two new alcohols identified by Hesse and Zeitschel in neroli and petitgrain oils. Nerol is isomeric with geraniol, and possesses a delicate odour of roses. It does not combine with calcium chloride, as does geraniol. Nerolidol is a sequiterpene alcohol, probably belonging to the aliphatic series. It has a feeble odour and the low specific gravity of 0.880.

[2] Indol and methyl anthranilate have been shown by Hesse and Zeitschel to be present in orange-flowers, and they are thus not accidental products of the process of manufacture.

[3] Methyl ortho-amido-benzoate, or methyl anthranilate, was discovered in neroli oil by E. and H. Erdmann and Schimmel & Co., and is an oil which crystallises on cooling. This body has been found by E. J. Parry in bitter orange oil, the crystals melting at 23° to 25°. It is interesting as being almost the only nitrogenous constituent of essential oils possessing a sweet odour. The artificial neroli oil of commerce consists chiefly of methyl anthranilate with various alcohols, and is a frequent adulterant of the natural oil.

the paraffin. The adulteration of neroli oil with stearoptene-free oils of course lowers the content of stearoptene and thus the strongly cooled oil may not become turbid, as would be the case with an oil containing a normal amount of the paraffin. This fact has been employed as a test for the genuineness of neroli oil.

CHINESE NEROLI OIL is stated to be derived from *Citrus triptera* (*Trifoliata*). An examination of this oil by Umney and Bennett (*Pharm. Jour.*, 1902, p. 146) showed that it is of a yellowish-brown colour, becoming paler on exposure to light. It has a sweet odour and is slightly fluorescent, this property being very readily observed in alcoholic solution. The specific gravity of Umney and Bennett's sample was 0.850, and it had an optical rotation of +35° for 100 mm. The oil contained 4.8 per cent. of esters calculated as linalyl acetate, and 21.4 per cent. of free alcohols (as linalol). It consisted chiefly of limonene; camphene (?); linalol; traces of linalyl acetate; methyl anthranilate; and a paraffin. The oil may be advantageously used for toilet- and soap-perfumery.

ORANGE-FLOWER WATER is usually obtained by the distillation of the flowers either with steam or water over an open fire. Oil of neroli and orange-flower water are obtained. The water reproduces the odour of the flowers much better than the neroli oil.

About one-third of the odoriferous constituents (and these the most valuable) of the blossoms pass into the water. Except for the terpenes, orange-flower water contains the same constituents as neroli oil, together with esters of phenyl-ethyl alcohol and, possibly, phenyl-aceto-nitrile. The proportions of free alcohols and of methyl anthranilate are much higher in the oil contained in orange-flower water than in neroli oil, while the esters of the terpene-alcohols are much less in amount. Orange-flower water is official in the British and United States Pharmacopœias.

Methods for the examination of *orange essences* have been published by Wender and Gregor (abst. *J. S. C. I.*, 1900, p. 372).

Parsley Oil.

This oil may be obtained by the distillation of any part of the common parsley herb (*Petroselinum sativum*). It is usually distilled from the seeds, but the finest oil is that obtained from the green herb.

The characters of parsley oil as obtained from different parts of the herb are shown in the following table. The specific properties and composition of French oil of parsley are also included:—

Source, &c.	Specific Gravity.	Optical Rotation ° in 100 mm. Tube.	Other Characters and Constituents.
Seeds, ...	1.05 to 1.10	—5 to —10	A colourless, yellowish or yellow-green thick oil, containing lævo-pinene and apiol.
Green leaves, ...	0.900 to 0.925	+0.2 to +3.2	Thin greenish-yellow oil, containing about 20 per cent. apiol.
Dried root, ...	1.049	*Dextro-rotatory*	*Apiol crystallises out at ordinary temperatures.*
French oil, ...	1.017	—5.7°	Palmitic acid (?); mixture of several phenols; pinene; myristicin; apiol. Myristicinic acid formed on oxidation.

Parsley oils containing much apiol (frequently called "parsley camphor") often become semi-solid, or deposit crystals, at the ordinary temperature. The apiol can be crystallised out from any oil containing it by cooling to a low temperature.

Apiol has the constitution of a dimethyl-methylene-ether of allyl-tetroxy-benzene. An isomer of this substance, dill-apiol, is present in oil of dill. The constitution and characters of these bodies are discussed on page 357 *et seq.*

Parsley oil has been found by Mourgnes, and by Bignami and Testoni (*Pharm. Jour.*, 1900, p. 313), to contain another constituent or mixture of constituents, to which Mourgnes gave the name "cariol." According to Bignami and Testoni, about 50 per cent. of this substance consists of a compound probably having the following constitution: $C_6H_2.(OCH_3).O.O.CH_2:(C_3H_5)$. This compound is possibly identical with the "myristicin" found by H. Thoms to be the chief constituent of French parsley oil (with some apiol), apiol being, according to this observer, the preponderating constituent of German parsley oil. Thoms gives the following formula as representing the constitution of the "myristicin"[1] isolated by him from French parsley oil:— $C_6H_2.(C_3H_5)^{(1)}.O.O.CH_2^{(3)(4)}.(OCH_3)^{(5)}$.

Peppermint Oil.

The English and American varieties of this important oil, which is official in the British and American Pharmacopœias, are obtained by the distillation with steam of the leaves and flowering tops of the herb *Mentha piperita.* The English oil is prepared from the green herb, while the best kind of American oil (from Wayne County, New York) are frequently obtained

[1] H. Thoms considers this compound to be true myristicin, while the similar compound in oil of mace (p. 435) he regards as *iso*-myristicin.

from the dried or partially-dried herb. Japanese and Chinese oils of peppermint are derived from *Mentha arvensis.*

Two varieties of the herb—known as black and white mint—are used in England for the production of oil of peppermint. The black mint is the coarser kind and yields more oil, of somewhat less delicate aroma, than the white mint.[1] Peppermint oil is much used in medicine and pharmacy, and in the preparation of confectionery and liqueurs.

The British Pharmacopœia describes peppermint oil as colourless, pale yellow, or greenish-yellow when recently distilled, becoming gradually darker by age.[2] The oil has the odour of the herb and a strong, penetrating, aromatic taste, followed by a sensation of coldness in the mouth. The Pharmacopœia directs that the oil should have a specific gravity of 0.900 to 0.920, and should dissolve in four volumes of 70 per cent. alcohol. It is further directed that if a portion of the oil be cooled to 17° F. (=—8.3° C.) and a few crystals of menthol be added, a considerable separation of menthol should take place.

English oil of peppermint is probably the finest in odour, although certain German distillates approach it in this respect. The odour and taste of the oil are very good guides to its quality. Peppermint oil improves in odour on keeping, even for many years.

American oil of peppermint is the only variety of this oil the composition of which is at all fully known, but so far as the other kinds have been examined, they have been found to closely resemble the American, and this is especially the case with the English oil. American oil of peppermint was the subject of an exhaustive research in 1894 by Power and Kleber (*Arch. Pharm.*, ccxxxii, p. 639), who found it to contain the following bodies: menthol; menthyl acetate; menthyl isovalerate; a menthyl ester containing $C_{10}H_{19}.C_8H_{11}O_2$; menthone; acetic aldehyde; acetic acid; isovaleric aldehyde and acid; inactive (?) pinene; *l*-limonene; phellandrene; cadinene; cineol; a lactone, $C_{10}H_{16}O_2$; traces of amyl alcohol and dimethyl sulphide; and some unstable high-boiling sulphur compounds. In addition, peppermint oil possibly also contains liquid isomeric menthols. The composition and quality of the oil are

[1] J. C. Umney found two oils from "black" and "white" mint to have the following characters:—

Source.	Specific Gravity.	Optical Rotation for 100 mm.	Menthol. Free. Combined. (per cent.)	Menthone. (per cent.)
Black mint........	0.9036	—23.5°	59.4; 3.7	11.3
White mint,........	0.9058	—33°	51.9; 13.6	9.2

[2] Japanese oil of peppermint is, however, at the ordinary temperature frequently a mass of crystals (menthol) saturated with oil.

considerably influenced by the climate and soil, and the cultivation methods employed.

P. Charabot has shown that during the development of the peppermint plant, an oil rich in menthol is first formed containing only a little ester and menthone. Later, the development of the green parts causes a diminution in the total menthol in the oil, while the esters increase in the leaves and diminish in the flowering part of the plant. Finally the menthone increases in the flowers by the oxidation of menthol. The esterification is confined to the green parts of the plant.

The specific gravity of pure English oil of peppermint is generally well within the B. P. limits, ranging usually from 0.906 to 0.909. Some pure specimens exceed these narrow limits, while very rarely a specific gravity of 0.925 is reached. American oils have specific gravities ranging from 0.910 to 0.920, while the density of French oils ranges from 0.918 to 0.921. German oils show a still higher specific gravity. Japanese oil from *Mentha arvensis* has usually a specific gravity of 0.895 to 0.900 at 24° C.

The optical rotation of English peppermint oil usually ranges from —27° to—32° (*U. S. Pharm.* limits = —25° to —33° at 25° C.) falling very rarely to —10° or lower. The rotation is least in the case of South Italy and French oils (about —5° to —10°) and greatest with the Japanese variety (up to about —43°). The British Pharmacopœia does not give any figures for this constant, which is, however, of much value, when taken in conjunction with specific gravity, &c., for the detection of adulteration.

The table on the next page shows the characters of normal peppermint oils from various sources.

Valuable figures relating to the physical characters and chemical composition of the various peppermint oils of commerce have been recorded by J. Lifschitz, *J. S. C. I.*, 1901, p. 151; Italian oils, C. E. Zay, *Chem. Centr.*, 1903, i, p. 331; abst. *J. S. C. I.*, 1903, p. 317; while Umney and Bennett have described the characters of Sicilian oils obtained from the black Mitcham peppermint herb grown in Messina (*Chem. and Druggist*, 1905, p. 945).

The solubility test for peppermint oil described in the British Pharmacopœia is not always fulfilled by pure oils (p. 447). Many oils dissolve in four volumes of 70 per cent. alcohol with at most a trifling opalescence, but the best kinds of American oil (from the dry herb, for instance), are not clearly soluble in alcohol of this strength. All the oils of peppermint are soluble in half or more volumes of 90 per cent. alcohol.

The U. S. Pharmacopœia requires peppermint oil to be rectified and free from dimethyl sulphide, the presence of which

CHARACTERS OF NORMAL PEPPERMINT OILS.

	American.		English. [Mitcham.]	French.	Russian.	Japanese.	Saxon (and Best German).	Italian (Refined). One Sample.
	Wayne County.	Michigan.						
Botanical Origin, ..	*Mentha piperita.*	*Mentha piperita.*	*Mentha piperita.*	...	...	*Mentha arvensis.*	...	...
Specific Gravity, ...	.910 to .920	.905 to .913	.900 to .910	.918 to .921	.905 to .915	.895 to .900 at 24° C.	.900 to .915	.912
Optical Rotation, ° .	—25 to —33	—18 to —29	—22 to —33	—6 to —8.5	—17 to —22	—25 or —30 to —43	—25 to —33	—16.3
Solubility in alcohol, 70 %, ...	Not clearly soluble.	Sol. 1 in 5.	Sol. 1 in 3 to 5.	Insol. (one sample).	...	Sol. 1 in 3 to 5.	(Fresh herb), sol. (Dry herb), insol.	Sol. 1 in 7.
Iodine Absorption, .	...	...	58	...	...	...	...	147
Solidification-point, ° C., ...	...	...	...	...	...	+17 to +28	...	...
Refraction index at 20° C., ...	...	1.4635	...	...	...	...	...	1.4680 at 16°
Effect of freezing, ..	Solid mass of crystals.	Solid mass.	Some crystals on long standing.	...	Some crystals on long standing.	At 15° mass of crystals saturated with oil.	Some crystals on long standing.	Does not congeal.
Total menthol, %, .	50 to 60	60	58 to 70	44 to 46	50	70 to 91	55 to 68	55.5
Free menthol, %, .	40 to 45	50	50 to 60	36 to 40	47	65 to 85	46 to 61	45.8
Combined menthol, %, ...	8 to 14	10	3 to 14	5 to 10	3; 14	3 to 6	6 to 8	9.7
Menthone, %, ...	12	...	9 to 12	8.8 to 9.6	(?) 35 to 40	...	16	8

may be recognised by the formation (after a short time) of a white film at the zone of contact when the first cc. of distillate from 25 cc. of the oil is poured on to a little mercuric chloride solution.

The normal composition and properties of the chief varieties of peppermint oil are given in the table on page 449. Japanese oil contains naturally a very high proportion of menthol—frequently as much as 85 per cent.—and dementholised (or partially dementholised) Japanese oil (by freezing) is sold sometimes as such, and sometimes as the pure oil. Dementholised Japanese oil has a specific gravity of 0.895 to 0.905 at 15°. English peppermint oil contains about 55 to 70 per cent. of menthol (free and combined), or somewhat more than the proportion found in most American oils. In the case of Japanese peppermint oils, a considerable separation of menthol crystals takes place at the ordinary temperature. American oil generally sets quite solid when placed in a freezing mixture, while English and German oils usually only deposit crystals after long standing in a freezing mixture. For this reason the British Pharmacopœial test for the presence of a due proportion of menthol, based on the separation of the crystals as already described, is no criterion of the value of the oil. The U. S. Pharmacopœia (8th Rev.) requires peppermint oil to contain at least 8 per cent. of ester (as menthyl acetate) and 50 per cent. of total menthol (free and combined), when assayed by the saponification and acetylation processes (see below).

Owing to its importance and high price, peppermint oil is extensively adulterated. An examination of the physical constants of the oil will serve to detect such additions as alcohol, and turpentine and some other oils. All adulterants cause a diminution of the menthol content,[1] which should therefore be determined. The methods for the determination of the free and combined menthol, by saponification and acetylation, and for the determination of menthone, by reduction with sodium to menthol and the subsequent determination of the alcohol formed, are fully described on page 229. The alcohol solubility figures are valuable, since it is frequently possible to determine the source of the oil by their means. In many cases where the oil is insoluble in 70 per cent. alcohol, a low menthol content will be found.

The behaviour of peppermint oils on distillation is a useful confirmatory test as to their genuineness. The published figures vary to some extent according to the method of distillation employed. It may be said, however, that all genuine oils

[1] It has, however, been stated that some oils, otherwise pure, have received an addition of menthol itself, which is frequently cheaper than oil of peppermint.

will yield a considerable fraction distilling in the neighbourhood of 215° C., since menthol boils at 212°. The following is a summary of the results of distillation (50 cc.) of 17 pure peppermint oils from various sources, recorded by Schimmel & Co.:—

Temperature.	Distillate. (Per cent.)
Up to 200° C.,	1.0 to 8.8
200°–205°	0.6 to 19.2
205°–210°	2.4 to 26.8
210°–215°	13.0 to 49.4
215°–220°	6.4 to 34.4
220°–225°	0 to 23.6
225°–230°	0 to 9.6
230°–235°	0 to 6.2
Residue,	4.2 to 17.4

Peppermint oil adulterated with light camphor oil will be found to give abnormally large fractions between 200° and 205° C. Parry and Bennett (*Chem. and Druggist*, 1903, p. 154) have called attention to the widespread adulteration of peppermint oil practised at the present time. They isolated from many samples of adulterated oils a high boiling fraction (258° to 268° C.) consisting mainly of cadinene, and they concluded that the adulterant was African copaiba oil. Such an addition lowers the rotatory power (or the sample may even be dextro-rotatory), raises the refractive index, and of course lowers the menthol-content.

Another adulterant of oil of peppermint, identified by C. T. Bennett (*Chem. and Druggist*, 1903, p. 591), is purified "acetin," a mixture of the three (mono-, di-, and tri-) acetic esters of glycerol, which was present to the extent of about 15 per cent.[1] The adulterant was obtained in the residue after distillation under reduced pressure. This residue was optically inactive, and had a specific gravity of 1.166 and a refractive index of 1.4355. A sample of the mixed acetins prepared by Bennett had a specific gravity of 1.187 and a refractive index of 1.4442. Pure oil of peppermint gives no fraction having a higher specific gravity than about 0.960, nor refractive index much outside the limits 1.461 to 1.479. Oils containing triacetin do not respond to the alcohol solubility test, since although soluble at first, on addition of more 70 per cent. alcohol oily drops separate on standing.

Still more recently, Parry and Bennett have described (*Chem. and Druggist*, 1904, p. 854) the adulteration of peppermint oil with cedar-wood oil. Three samples showed a specific gravity

[1] Commercial acetin is used as a solvent for indulin and other colouring matters used in calico printing, and generally contains free acetic acid and glycerin. It is prepared by heating together a mixture of glycerin and glacial acetic acid for several hours.

of 0.908, an optical rotation of —24°, a refractive index of 1.4670 at 20° C., and a total menthol content of 48 to 49 per cent. The oils were insoluble in 70 per cent. alcohol, from 30 to 50 per cent. floating on the surface of the liquid. Fractional distillation revealed the presence of cedar-wood oil by the increasing specific gravity, optical rotation, and index of refraction of the later portions of the oil. By refractionation of the last 5 per cent. distilled, Parry and Bennett obtained fractions showing specific gravities ranging from 0.914 to 0.933; optical rotation, —40° to —45°, and refractive index, 1.470 to 1.500. Certain of these fractions had a distinct cedar-wood taste.

Various colour-reactions of oil of peppermint have been described, which are, however, of very little if any use as tests of purity. The best known reaction is that produced by the action of glacial acetic acid on English and American oils. Japanese oil of peppermint does not respond to the test. When about 5 drops of the oil are mixed with 1 cc. of glacial acetic acid, a blue colour is obtained (after several hours), which gradually increases in intensity up to 24 hours.[1] In the case of American peppermint oil a dark blue colour is seen when viewed by transmitted light, and a fine copper-coloured fluorescence with reflected light. The English oil gives a similar though less pronounced reaction. Slight warming of the mixed liquid accelerates the reaction, a violet-blue then resulting. The body causing the reaction is stated by Polenske to be a non-nitrogenous volatile substance. The reaction is an oxidation, since it only takes place in presence of air. Oils previously exposed for some time to sunlight do not give the reaction. (See further P. Welmans, *Pharm. Zeit.*, 1901, p. 591; abst. *Analyst*, 1902, p. 277.)

Spirit of Peppermint (*Spt. Menth. Pip.*, *B. P.* and *U. S. P.*) and essence of peppermint, for which the pharmacopœial preparation is generally supplied, is a solution of one part by measure of peppermint oil in 9 parts of 90 per cent. alcohol.

Spearmint Oil.

The British Pharmacopœia describes this oil as being obtained by distillation from the fresh flowering spearmint, *Mentha viridis*. American oil is obtained from this source, whilst the German oil is obtained from *M. crispa*. The botanical source of Russian oil of spearmint is doubtful.

[1] The reaction may be very quickly produced by operating in the manner described in the U. S. Pharmacopœia (1890). Two cc. of the oil is mixed with 1 cc. of glacial acetic acid and 1 drop of nitric acid. Under these conditions even Japanese oil gives a slight violet coloration.

Spearmint oil is colourless, pale yellow, or greenish-yellow when recently distilled, becoming darker with age. It has the odour and taste of the herb. The British Pharmacopœia states that the oil has a specific gravity of 0.920 to 0.940, and forms a clear solution with its own volume of 95 per cent. alcohol. With 80 per cent. alcohol the oil forms a clear solution in equal volumes, but turbidity is produced on further dilution with the alcohol (U. S. Pharmacopœia, 8th Rev.).

The following table shows the characters of the various oils of spearmint, &c., based mainly on the results of Schimmel & Co. Only the first two oils are of any practical importance:—

Kind of Oil.	Botanical Source.	Specific Gravity.	Optical Rotation ° in 100 mm. Tube.	Other Characters.
American, .	*Mentha viridis.*	.920 to .940	—36 to —48	Sol. in equal vols. of 90 per cent. alcohol. Contains lævo-carvone and *l*-limonene, &c.
Russian, . .	*M. aquatica* (?).	.880 to .890	—20 to —25	Sol. in 2 vols. 70 per cent. alcohol. Contains lævo-carvone; *l*-linalol; *l*-limonene; and cineol.
	M. aquatica.	.880 to .890	variable.	
	M. Canadensis.	.940	. . .	
Horsemint,	*Monarda Punctata.*	.930 to .940	Slightly +	Contains terpenes; cymene; thymol; linalol (?); traces of acetic, butyric, and other fatty acids.

Oil of spearmint contains lævo-pinene, *l*-limonene, carvone and probably small amounts of linalol and other substances. The proportion of carvone varies from about 35 to 55 per cent. It may be determined as described on page 382. Russian oils appear to contain cineol in addition. The odoriferous constituent of spearmint oil is unknown.

Schimmel & Co. have described a spearmint oil (distilled by them in America) which had a specific gravity of 0.980 and an optical rotation of —42.5°. It appeared to contain an abnormally large amount of carvone.

Oil of Pennyroyal of commerce is derived from the leaves and other parts of the fresh herb, *Mentha pulegium,* and is a yellow or reddish-yellow oil of a strong minty odour. It ranges in specific gravity from 0.930 to 0.960, and in optical rotation from +16 to + 25° in 100 mm. tube. The oil is soluble in two or more volumes of 70 per cent. alcohol.

Pennyroyal oil contains menthol, pulegone, α- or β-isopulegone (possibly), menthone, and terpenes (probably lævo-limonene and dipentene). About 80 per cent. of the oil distils between 212° and 216° C. Adulteration with turpentine oil

lowers the specific gravity and boiling-point of pennyroyal oil, while it is less soluble in alcohol when this adulterant is present.

Russian oil of pennyroyal is derived from *Pulegium micranthum,* and has a specific gravity of about 0.930. American pennyroyal oil is the product of the herb *Hedeoma pulegoides,* and has characters similar to the ordinary pennyroyal oil.

Pimento Oil. ALLSPICE OIL.

This oil is obtained by the distillation of the dried unripe fruit of *Pimenta officinalis.* It is yellow or yellowish-red oil becoming gradually darker in colour. It has the odour and taste of pimento, which resembles a mixture of cinnamon, nutmeg, pepper, and cloves, the last-mentioned predominating. Hence the name "allspice," from the mixed odour of the fruit.

The British Pharmacopœia gives the specific gravity of pimento oil as not below 1.040.[1] It states that "the oil should be converted into a semi-solid mass when shaken with an equal volume of strong solution of ammonia." In the U. S. Pharmacopœia, strong caustic soda solution takes the place of ammonia.

Pimento oil consists for the most part of eugenol, which is present to the extent of about 65 to 70 (or even 80) per cent. In addition, the oil contains cineol, *l*-phellandrene, methyl-eugenol, &c. A sesquiterpene is also present, but its exact nature has not yet been fully ascertained. The odoriferous body or bodies are unknown. The oil closely resembles oil of cloves in composition and properties.

The specific gravity of genuine oil of pimento usually varies from 1.040 to 1.055. The optical rotation ranges from —1° or —2° to —4°.

Fractional distillation is a valuable aid in judging of the purity of this oil. The specific gravity is higher according as the eugenol-content is higher, and the fraction distilling over between about 245° and 250° C. should be large, as it contains the whole of the eugenol, which boils at 247° C. The proportion of eugenol, as determined by Thoms' method (page 362) should be at least 60 to 65 per cent. The U. S. Pharmacopœia (8th Rev.) requires the oil to contain at least 65 per cent. by volume of eugenol when assayed by Umney's process (see page 361).

[1] Schimmel & Co. give the limits of specific gravity of this oil as 1.024 to 1.050, and state that the B. P. limits require correction. The experience of English chemists, however, agrees with the limits laid down by the Pharmacopœia, and it seems improbable that an oil of 1.024 sp. gravity can contain a due proportion of eugenol.

Oil of pimento is soluble in all proportions in 90 per cent. alcohol, and also in two volumes of 70 per cent. alcohol.

OIL OF PIMENTO LEAVES has been described by Gildemeister and Hoffmann as having a specific gravity 0.882 at 25° C., and an optical rotation of —0.6° for 100 mm. The oil has a strong citron-like odour, and contains citral.

Pine-needle Oils.

Under the above title are comprised the volatile oils of the needles and young shoots of various coniferous plants. They are all colourless liquids of pleasant balsamic odour. In composition they present a strongly marked contrast to the different varieties of turpentine oil, having a distinct aromatic odour and yielding only a small percentage of distillate below 170° C. The most characteristic constituent of pine-needle oils is bornyl acetate, though other esters of borneol appear to be present in some varieties. In addition, pine-needle oils contain various terpenes, mostly lævo-rotatory, among which lævo- and dextro-pinene, lævo-limonene, dipentene, phellandrene and sylvestrene have been recognised. The oils of this class are used to a considerable extent in medicine and pharmacy, and in the arts. The table on page 456 shows the characters of the chief pine-needle oils, the data being taken from the researches of Bertram and Walbaum (Schimmel & Co., *Report*, Oct., 1892; *Archiv. der Pharm.*, 1893, ccxxxi, 291) and from the recorded results of Gildemeister and Hoffmann (*The Volatile Oils*). The characters of certain factitious oils examined by the first-named observers are also included in the table:—

From the foregoing figures it appears that pure pine-needle oil yields on distillation only a moderate fraction (pinene, &c.) below 170° C., and leaves a considerable portion undistilled at 185°. This residue consists chiefly of bornyl acetate and other esters of borneol.

Sample 4, a pine-twig oil from *Abies excelsa* or *pectinata*, contained no appreciable quantity of borneol or its derivatives (0.5 per cent.), the oil consisting almost entirely of lævo-pinene and lævo-limonene, which latter constituent was recognised by the melting-point of the hydrobromide (104° C.)

The so-called American Hemlock or Spruce oil (No.12) contained 36 per cent. of bornyl acetate, the other constituents being lævo-pinene and a sesquiterpene (cadinene).

The oil from *Pinus nigra* is stated by E. Kremel to contain over 50 per cent. of bornyl acetate. The esters of homologues of acetic acid are probably present in certain pine oils.

Pumilio oil (Pine Oil), which is official in the British Phar-

CHARACTERS OF PINE-NEEDLE OILS.

	Specific Gravity. 15.5° C.	Optical Rotation. (100 mm.)	Solubility in Alcohol (90%).	Esters as Bornyl Acetate. Per Cent.	Behaviour on Distillation, ° C.			
					First distillate at	150 to 170° Per Cent.	170 to 185° Per Cent.	Residue. Per Cent.
Genuine Pine Oils:—								
1. From needles and twigs of *Picea vulgaris* (Norwegian Spruce),	0.880 to 0.888	—21.7 to —37	...	8.3 to 9.8	160°	20	50	30
2. From needles and twigs of *Abies alba* (Miller). (*Abies pectinata*; Silver Fir),...	0.869 to 0.875	—20 to —59	1 : 5	4.5 to 11	...	8	55	37
	0.885	—35	1 : 6.5	6.1	162°	...	55 (Limonene.)	...
3. From cones of *Abies alba* (Miller) (fir-cone oil),...............	0.853 to 0.870	—60 to —76	1 : 6	0.5 to 4	...	11	37 (Limonene.)	52
4. From twigs of *Abies alba* (*A. pectinata*),..	0.854	—72.4	...	(No borneol.)	...	16	76	8
5. Needles and young twigs of *Pinus pumilio* (Haenke) (*Pinus Montana*),..........	0.865 to 0.875	—4.5 to —9	...	5 *to* 7	170°	...	70 (to 180°)	30
6. Needles of *Pinus sylvestris* (English),..	0.885 to 0.889	—7.7 to —19	...	2.9 to 3.5	...	8 *to* 13	33 to 47	...
7. Needles of *Pinus sylvestris* (German),..	0.884 to 0.886	+7 to +10	1 : 10	3.2 to 3.5	160°	10	46	44
8. Needles of *Pinus sylvestris* (Swedish),..	0.872	+10.7	...	3.5	160°	44	40	16
9. Needles of *Pinus cembra* (Siberian Cedar),............	...	+29.1	...	...	...	...	...	...

10. Needles and twigs of *Abies Siberica* (Siberian). (*Larix Siberica*),.............	0.905 to 0.920	—40 to —42	1 : 1	35	...	...	...	...
11. Needles of *Picea nigra* (Black Spruce),	0.922 (20°)	—36.4	...	48.8		(Chiefly at 212° to 230°.)		
12. Needles and young twigs of *Abies Canadensis* (hemlock); *Picea alba* (White Spruce); and *Picea nigra*. (Mixed distillate.) [Hemlock or Spruce Oil],.........	0.907 to 0.913	—21 to —24	...	36	...	11	37	52
13. Fresh twigs and young cones of *Balsam Fir*. (North America),..........	0.888 (20°)	—28.9	...	17.6	...	49	29	22
14. Needles of *Larix decidua* (Larch),.......	0.878	+0.7	1 : 5	8.1	...	54	24 (to 190°)	22
FACTITIOUS OILS:—								
A....................	...	+14	...	...	...	96	1	3
B....................	0.873	+4	...	...	...	95	1	4
C....................	0.868	Inactive.	...	...	...	100	...	...

macopœia (1898),[1] contains smaller proportions of pinene and borneol derivatives, but the presence of phellandrene is indicated by the ready formation of its nitrite. Sylvestrene and cadinene are also present. In the Austrian Alps, the needles and branches of *P. pumilio* are distilled on a large scale, and the oil obtained is used extensively in soap-making and perfumery. A sample of 0.865 specific gravity, and —9° rotation contained lævo-pinene and *l*-phellandrene, sylvestrene, bornyl acetate (5 per cent.) and cadinene. The oil produced in Sweden from the needles of *P. sylvestris* (No. 8 in table) contained dextro-pinene, sylvestrene, and probably some bornyl acetate.[2] The German oil from the same tree had a similar composition.

Bertram and Walbaum conclude that pinene is generally present in pine-needle oil, but that while the oils from *Abies picea* contain chiefly lævo-pinene, the product of the ordinary fir contains the dextro-modification.

Of the *factitious pine oils* represented in the table, A and B consisted substantially of ordinary turpentine oil with a small addition of true pine-needle oil, while C contained ethyl acetate which distilled as a first running below 150° C.

Rose Oil. Otto of Roses. Attar of Roses.

This essential oil, so important to the perfumer, is obtained from the fresh flowers of *Rosa Damascena*, *R. centifolia*, *R. alba*, and other varieties and is chiefly distilled in Bulgaria. The oil has suffered extensively in the past from adulteration, and both the Bulgarian distillers and the Turkish dealers sometimes add palmarosa oil (Turkish geranium) and other products. An examination of the "odour" of rose otto is still one of the best guides to purity.

Rose oil deposits at ordinary temperatures a variable amount of stearoptene as a crystalline mass. The white rose yields a somewhat larger quantity of stearoptene than the red rose. At temperatures slightly higher (20° C.), rose oil is a pale yellow fluid. Its specific gravity at 15.5° is 0.860 to 0.870, and about 0.848 to 0.858 at 30° (rarely above .856). The Brit. Pharm.

[1] The oil from *Pinus sylvestris* was official in the British Pharmacopœia (1885). The oil from *P. pumilio* replaced it in the 1898 edition, since the former oil is not now met with in commerce. Not more than 10 per cent. of pumilio oil should distil below 165° C. (B. P., 1898). The Pharmacopœial limits for specific gravity (0.865 to 0.870) are somewhat too narrow.

[2] According to Tröger and Bentin (*Pharm. Jour.*, 1904, p. 900) the oils distilled from the young shoots of *P. sylvestris* and *P. strobus* contain dextro- and lævo-pinene respectively, but are free from sylvestrene, cadinene and the borneol esters present in the oils from older leaves, which compounds are thus produced in later growth.

(1898) states that rose oil (which according to that authority should be distilled from *R. Damascena*) has a specific gravity of 0.856 to 0.860 at 30° C. and congeals and melts at from 19.4° to 22.2° C. (=67° to 72° F.). These requirements are very misleading and inadequate. The congealing and melting-points of the oil vary according to the proportion of stearoptene present.

Rose oil is only slightly optically active, the mean rotation being about —3°. Some few German oils are faintly dextrorotatory (+1°).

The constituents of rose oil have probably been the subject of more controversy than those of any other oil. It has been known for many years that rose oil and oils of the geranium variety contain an alcohol, $C_{10}H_{18}O$, to which *Jacobsen* in 1870 gave the name "geraniol." *Bertram* and *Gildemeister* then recognised that rose oil contained a mixture of two alcohols, of which geraniol, $C_{10}H_{18}O$, was the chief. *Tiemann* and *Schmidt* finally proved the identity of the other alcohol with that obtained by *Dodge* in 1890 by reduction of citronell-aldehyde.[1] This alcohol is citronellol, $C_{10}H_{20}O$. Much confusion has arisen on account of the numerous names which have been given by the various workers on the subject to one or other of these two alcohols. Many of these names have now been abandoned, as most of the products have been found to consist of geraniol and citronellol in varying proportions. Thus the "rhodinol" of *Erdmann* and *Huth*, and the "lemonol" of *Barbier* and *Bouveault* consist of geraniol; the "rhodinol" of *Eckart*, the "roseol" of *Marknovnikoff* and *Reformatsky*, and the "réuniol" of *Hesse*, are mixtures of geraniol and citronellol; whilst the "rhodinol" of *Barbier* and *Bouveault*, and the "réuniol" of *Naschold*, are identical with citronellol. Substances sold in commerce under the names of "rhodinol"[2] and "réuniol" are mixtures of geraniol and citronellol.

The principal constituents of both Bulgarian and German oil of roses are, therefore, the alcohols geraniol and citronellol. These alcohols are present in the oil in the proportion of 75 per cent. of geraniol to 25 per cent. of citronellol. German oils, however, contain less citronellol than Bulgarian oils.

The presence of geraniol in oil of roses (and also in African geranium oil) may be shown by treating the liquid portion of the oil with calcium chloride, when the characteristic crystalline

[1] Citronellol from oil of roses is, however, lævo-rotatory to the extent of —4.3° in a 100 mm. tube.

[2] Commercial "rhodinol" consists of a mixture of 30 to 40 per cent. of citronellol and 60 to 70 per cent. of geraniol. "Licarhodol" was the name given by Barbier to a product obtained by heating linalol with acetic anhydride. According to Schimmel & Co., it consists of geraniol and dextro-terpineol.

geraniol-calcium chloride compound is produced (see page 328). Citronellol does not form a corresponding compound. Another method of detecting the presence of geraniol in essential oils is to isolate the diphenyl-urethane derivative (page 330), which crystallises in colourless needles melting at 82° C. Citronellol diphenyl-urethane is an oily, non-volatile body. Citronellol is determined in rose oil by formylating a mixture of 1 volume *of oil with 2 volumes of 100 per cent. formic acid, heating for one hour over a reflux-condenser. The method is then conducted as in the acetylation of oils* (page 229). Other processes for the detection and determination of the open-chain alcohols in rose oil, &c., are described in detail on page 332 *et seq.*

In addition to the two chief alcoholic constituents and the stearoptene, already described, there exist in rose oil other bodies which, although present in small quantity only, nevertheless appreciably modify the odour of the oil. Thus traces of esters of geraniol and citronellol occur, together with acids produced by slight decomposition.[1] Walbaum and Stephan *have proved the presence of normal nonyl aldehyde, citral, and* linalol.[2] Erdmann *has shown normal phenyl-ethyl alcohol to* be present (partly as esters) and, according to Eckart, ethyl alcohol (5 per cent. of the liquid portion) is a normal constituent of the oil, but this is only present in the product from roses which have partially fermented before distillation (Poleck). Von Soden and Treff claim to have isolated nerol (5 to 10 per cent.), eugenol (1 per cent.) and a sesquiterpene alcohol ("farnesol"?), 1 per cent. Phenyl-ethyl alcohol is especially important as contributing to the odour of rose otto, but although this compound is present to a considerable extent in rose-flowers, *it only occurs in small amount in rose otto, being largely lost* in the distillation-water.

The *stearoptene* present in rose oil is apparently a mixture of two solid hydrocarbons, melting at 22° and 41° C. respectively. The mixed substance as it exists in the oil melts at 33° to 35° C. The proportion of stearoptene present in different oils varies within very wide limits, so that the amount of this constituent is no criterion as to the purity of the oil.[3]

The specific gravity of rose oil varies naturally between

[1] According to some observers an easily hydrolysed lævo-rotatory ester is present in the oil and to the decomposition of this ester is ascribed the acidity of rose-flower water.

[2] Schimmel & Co. prepare a synthetic "otto" based on the researches of Walbaum and Stephan.

[3] According to E. J. Parry, Bulgarian oils contain 10 to 20 per cent. of stearoptene, *while the oils from France, Germany and England are said to contain 25 to 60 per cent. Any oil containing a percentage of stear-*optene even approaching this higher figure cannot be regarded as a normal product.

fairly wide limits and according to the proportion of stearoptene. Adulteration of rose otto with alcohol causes a low specific gravity. The refractive index of otto of rose varies from about 1.4600 to 1.4655. Palmarosa oil has a refractive index of about 1.4745. The presence of alcohol (refractive index, 1.365) is suggested in the case of samples having a low refractive index, which figure is a useful factor in the examination of rose otto.

The congealing-point (setting-point) of rose otto may be determined in the following way (P. N. Raikow, *Chem. Zeit.*, xxii, p. 149):—About 10 cc. of the oil to be examined is placed in a test-tube of 15 mm. diameter, and the oil warmed by means of the hand until it attains a temperature well above the solidifying-point. A thermometer is meanwhile placed in the oil in such a manner that it touches neither the bottom nor sides of the tube, but has its bulb completely immersed. The oil is allowed to cool spontaneously, and the temperature at which the first crystals appear is the congealing-point. Duplicate determinations should be made. This method has been adopted in the U. S. Pharmacopœia (8th Rev.), which requires rose oil to congeal at a temperature between 18° and 22° C. (64.4° to 71.6° F.).[1]

Adulterated rose oil may contain paraffin-wax or spermaceti, which should be looked for in the separated solid portion of the oil. The stearoptene of rose oil usually melts at 33° to 34° C. and should not exceed the limits of 32° to 37° C. Higher melting-points indicate adulteration with paraffin-wax or spermaceti.

E. J. Parry states (*Chemistry of Essential Oils, &c.*) that while the detection of spermaceti and stearin in rose oil is comparatively easy, the detection of paraffin-wax or the solid constituent of "guaiacum-wood" oil[2] presents greater difficulty. On saponifying the stearoptene of the oil under examination, no fatty acids will be obtained if the oil is pure, while spermaceti and stearin yield palmitic and stearic acids (melting at 55°–62°

[1] The U. S. Pharmacopœia further requires rose oil to have a specific gravity of 0.855 to 0.865 at 25° C., and to show a saponification value of not less than 10 nor more than 17 when treated by the usual Koettstorfer's process (see p. 229), about 2 cc. of the oil, accurately weighed, being used for the determination. The number of cc. of semi-normal alcoholic potash absorbed by the oil in the process, multiplied by 27.87 $\left(\frac{\text{Mol. Wt. KOH}}{2}\right)$ and divided by the weight of oil taken, gives the saponification-value of the oil.

[2] According to E. P. Paetzold, the so-called concrete oil of guaiacum-wood is the product of *Bulnesia sarmienti*, and is one of the chief adulterants of Turkish rose oil. It is used especially in conjunction with geranium oil. It has a mild tea-like odour, and consists largely of a crystalline alcohol of melting-point 91° C., and is thus semi-solid at the ordinary temperature. The oil is stated to have a specific gravity of 0.969 at 35°, and an optical rotation of —6.7° (100 mm.).

and 62°–68° respectively). Paraffin-wax may be detected by its more granular crystalline structure as compared with the rose stearoptene. The alcoholic body from guaiacum-wood oil will yield an acetyl-number. Antipyrin is occasionally found as an adulterant of rose-otto.

The following figures show the physical characters of different varieties of rose oil, as recorded by various observers:—

Variety of Rose Oil.	Observers.	Specific Gravity (° C.).	Rotatory Power ° in 100 mm. Tube.	Solidifying Pt., ° C.	Stearoptene (per cent.).
	Brit. Pharm., 1898.	.856–.860 (30°)	...	19.4–22.2	...
	U. S. Pharm.	.855–.865 (25°)	...	18–22	...
Bulgarian,	Dupont and Gueslau.	.865 (30°)	—3.5	...	6–13
Bulgarian,	J. C. Umney.	.856–.860 (30°)	...	20–21	16–18
Bulgarian,	M. Conroy.	.850–.856 (30°)	—2.3 to —2.7	...	...
Bulgarian,	E. J. Parry.	.848–.858 (30°)	—1.8 to —4.0	17–23	18–22.5
French, . . .	Schimmel & Co.	...	—7 to —9	...	...
French, . . .	Dupont and Gueslau.	.8225 (30°)	—6.8	...	35
		.8407 (30°)	—8.05	...	26
German, . .	P. N. Raikow.	.853; .858 (27.5°).	—2.7; —2.1	20.5; 22.5	...
German, . .	Schimmel & Co.	.837; .830	—0.75	29; 30	28.5; 40
Persian, . .	Schimmel & Co.	.832 (25°)	—9.1	21.5	...
Russian, . .	Bertrand Fils.	.836 (30°)	—4.2	23	33.5

The specific gravity of rose oil is not of much value when considered apart from other constants, since the several varieties of the oil differ to a not inconsiderable extent, and the varying content of stearoptene also causes a natural variation. According to J. C. Umney, a rose oil having a specific gravity exceeding 0.861 at 30° C. should be looked upon with suspicion. The figures for the optical rotation of rose oil and its adulterants do not show sufficiently well-marked differences to be valuable in determining the purity of rose oils.

The melting- and solidifying-points of genuine rose oils may be taken as lying between the limits 17° and 23°, although the percentage of stearoptene affects them. A high solidifying point indicates excess of stearoptene (or adulteration with paraffin-wax, &c., see page 461), while the odour of the oil will be correspondingly weakened. Oils adulterated with geranium oil have a lowered solidifying point and of course contain a decreased proportion of stearoptene. For the determination of the amount of stearoptene present in the oil, Schimmel & Co. (*Semi-Annual Report*, 1889) heat 50 grammes of the sample with 500 grammes of 75 per cent. alcohol to 70° to 80° C. On cooling the mixture to 0° C. the stearoptene separates almost quantitatively. The liquid is filtered, again treated similarly with 200 grammes of the alcohol, and this treatment is continued until the stearoptene is quite odourless. Two treatments of the crude stearoptene are usually sufficient, and the product is then dried and weighed.

According to F. Dietze, the acid and ester numbers of pure rose oils (in terms of per cent. KHO) range from 0.12 to 0.26 (acid number) and from 0.65 to 1.9 (ester number), while geranium oils show an ester number of 2.6 to 7.2. These constants are of very doubtful value as an indication of purity (see P. N. Raikow, *Chem. Zeit.*, xxii, 149; abst., *Analyst*, 1898, page 104).

The determination of the alcoholic constituents of rose oil (by the acetylation process, page 229) would appear to be of some value as a criterion of purity, in spite of many statements to the contrary. J. C. Umney found the finest ottos to contain 71 to 72.5 per cent. of total alcohols. High stearoptene-content lowers this figure, while admixture with geranium oil raises it considerably, and at the same time increases the specific gravity. Umney cites the following results (among others) obtained by the examination of genuine and adulterated samples of rose oil:—

	Genuine Oils.			Adulterated Samples.		
	1.	2.	3.	4.	5.	6.
Specific gravity, 30° C.,	0.857	0.860	0.861	0.863	0.868	0.868
Crystallising-point, ° C.,	20.9	20.4	20.0	19.4	18.7	18.9
Stearoptene, per cent.,	18	16	14	12½	10	10
Alcohols (as $C_{10}H_{18}O$),	70.1	72.3	73.1	75.6	77.6	76.6

Hudson-Cox and Simmons (*Analyst*, 1904, xxix, 175) recommend the iodine-absorption figure as a means for detecting adulteration of natural otto of rose with the synthetic product, and other substances. These observers employ 0.1 to 0.2 gramme of otto, adding 10 cc. of chloroform or alcohol (90 per cent.), and 25 cc. of Hübl's iodine solution. The excess of iodine in the mixture is titrated in the usual manner after the liquid has been allowed to stand for 3 hours in the dark at the ordinary temperature.[1] The following results, in addition to those recorded in the table below, were obtained in this manner:—Palmarosa oil, 296 to 307 per cent. of iodine absorbed; geranium oils: (African), 213 to 225, (Bourbon), 213 to 215, (Spanish), 211; citronella oil, 217; guaiacum-wood oil, 298; geraniol, 307 (?); citronellol, 187; linalol, 280; citral, 175; and

[1] A considerable variation in temperature has no appreciable effect on the results. Hudson-Cox and Simmons use only Hübl's solution of full strength, and therefore they consider it convenient and advisable to keep the iodine and mercuric chloride solutions separate, and mix them the evening before using. The titration should be carried out as rapidly as possible. It is noteworthy that while the artificial otto is almost deodorised by iodine, the natural otto is unaffected in this respect.

CHARACTERS OF GENUINE AND ARTIFICIAL ROSE OTTOS.

	Specific Gravity at 30°.	Optical Rotation, 30° C. (100 mm.).	Sapon. Number.	Solidifying Pt., ° C.	Iodine Absorption. Per Cent.	Remarks.
Genuine ottos (5 samples), ...	.851 to .859	—2.1 to —2.7	7.5 to 15.5	20.3 to 21.0	187 to 194	...
Genuine ottos (5 samples), ...	.852 to .856	—1.8 to —3.2	7.7 to 9.9	19.9 to 21.6	189 to 192	Refractive indices, 1.4613 to 1.4646.
Artificial Ottos:—						
With stearoptene (2 samples),......	.863; .859	—0.9; —0.2	20.5; 3.8	22.5; 21.9	(221 to 254)	...
Without stearoptene (2 samples),..	.872; .866	—1.3; —0.9	13.4; 5.7	...	(261 to 279)	...
Commercial Ottos:—						
No. 1..........................	0.855	—2.7	8.9	20.8	219	Probably contained geraniol.
No. 3..........................	0.855	—2.7	8.1	19.8	206	Probably contained artificial otto.
No. 4..........................	0.858	—1.4	10.3	21.3	234	Chiefly artificial otto.
No. 6..........................	0.843	—0.8	16.1	18.5	133	Contained much added alcohol.
No. 8..........................	0.855	—2.0	9.8	20.6	215	Mixture of 1 part artificial with 2 parts of genuine otto.

the stearoptene of rose oil, none. With the exception of citronellol and citral, all the iodine values largely exceed those of genuine otto of rose, the oils of citronella, which most closely resemble otto of rose in this respect, being readily recognisable by their ester-content.

The figures in the table (page 464) have been recorded by Hudson-Cox and Simmons (*loc. cit.*), and by W. H. Simmons (*Chem. and Druggist*, 1904, Oct. 22) for various samples of genuine and artificial ottos and their adulterants.

Jeancard and Satie (*Bull. Soc. Chim.* [3], 1904, xxxi, 934) found an oil distilled from the calyx, stamen and pistil of the rose to have the following characters:—Specific gravity, 0.8704 at 15.5° C.; optical rotation, —41° for 100 mm.; solidifying-point, +8° C.; acid number, 6.12; ester number, 22.4; stearoptene (chiefly a substance melting at 14° C.) 51.1 per cent.; and citronellol (the only alcohol present), 13.6 per cent.

Rosemary Oil.

This oil is distilled from the flowering tops of *Rosmarinus officinalis*. It is a pale yellow or colourless oil, having an odour of rosemary and a warm camphoraceous taste. The oil distilled from the dried leaves without admixture of stalks is the finest product, having a good odour and high borneol-content.

Oil of rosemary is official in the British and U. S. Pharmacopœias. It is described in the British Pharmacopœia (1898) as an oil of specific gravity 0.900 to 0.915, which dissolves in two volumes of 90 per cent. alcohol. It should have an optical rotation of not more than +10° in a 100 mm. tube. The latter constant guards against the presence of turpentine oil (see below). The U. S. Pharmacopœia requires rosemary oil to have an optical rotation of not more than 15° to the right, and to give a 10 per cent. fraction showing dextro-rotation.

The constituents of oil of rosemary are somewhat numerous and include camphor,[1] cineol, borneol[1] and its esters (chiefly bornyl acetate) and traces of dextro-pinene and camphene.

English oil of rosemary is more valued in commerce than either the French or the so-called Italian variety. The latter is the cheapest oil. It is actually produced in certain of the Dalmatian islands.

The *specific gravity of genuine oil of rosemary* (*English and foreign*) varies from 0.900 to 0.918, possibly occasionally to 0.920, and thus the Pharmacopœial limits are somewhat too

[1] A. Haller (*Compt. rend.*, cviii, p. 1308; abst. *J. S. C. I.*, viii, 1889, p. 1008) states that both dextro- and lævo-camphor and dextro- and lævo-borneol are present in oil of rosemary.

narrow.[1] The specific gravity is altered by the addition of oil of turpentine, with which rosemary oil is sometimes adulterated.

The optical rotation only rarely exceeds +10°, the British Pharmacopœia limit; E. J. Parry gives +1° to +12°. Dalmatian oils usually give figures between the limits of +1° to +4°. Spike oil is sometimes added to oil of rosemary, and this adulterant does not interfere with the specific gravity or optical rotation. It has recently been pointed out by Parry and Bennett that lævo-rotatory oils of rosemary are quite consistent with purity. These observers have found that the herb from Spanish and French sources may yield oils having either a lævo-rotation (—3°; —8.5°) or giving a lævo-rotatory first fraction (10 per cent.) on distillation (at 100 mm. pressure). These results are due to the lævo-pinene present naturally in the rosemary stems. (See *Chem. and Druggist*, 1906, page 671.)

Genuine oil of rosemary should be soluble in from ½ to 2 volumes of 90 per cent. alcohol, and in 2 to 10 volumes of 80 per cent. alcohol. The solubility of rosemary oil in alcohol is disturbed by adulteration with turpentine oil or the higher fractions of petroleum.

Rosemary oil is occasionally adulterated with alcohol, which may be detected by fractional distillation. Genuine oils do not give more than about 15 to 20 per cent. of distillate under 170° (at the ordinary pressure). A larger amount than this indicates the presence of alcohol or turpentine oil. The greater portion of rosemary oil distils between 175° and 200° C.

The proportions of esters and free alcohols are determined in the usual way (page 229). Calculated as borneol and bornyl acetate, the percentage of these constituents in genuine rosemary oils averages about 17 to 18 per cent. of alcohols, and 5 to 6 per cent. of esters.[2] The U. S. Pharmacopœia (8th Rev.) requires the oil to contain at least 5 per cent. of esters (as bornyl acetate) and at least 15 per cent. of total borneol.

[1] Schimmel & Co. (*Semi-Annual Report*, April, 1900) state that Spanish oil of rosemary has a higher specific gravity and greater optical activity than other kinds. A sample of this oil, examined by them and stated to be absolutely pure, was found to have a sp. gr. of 0.932; optical rotation, +17.5 at 20°; optical rotation of first 10 per cent. distilled, +4.75 at 20°. The oil was soluble in 2 volumes of 80 per cent. alcohol.

[2] The proportions of these constituents appear to vary between fairly wide limits. The lowest allowable limit for ester content might be placed at 4.5 to 5 per cent. (calculated as bornyl acetate), while 10 per cent. of alcohols (calculated as borneol) should be regarded as the lowest amount allowable, and probably 12 per cent. would be a fairer limit. Many oils contain considerably more alcohols than this, as stated in the text. J. C. Umney found three genuine oils to contain from 11 to 15 per cent. of alcohols.

Sandal-wood Oil. SANTAL-WOOD OIL.

There are many different varieties of this oil, since several plants of the natural order *Santalaceæ* are used for its distillation. The most valuable of these oils, and that which is official in the British and U. S. Pharmacopœias, is the East Indian sandal-wood obtained from *Santalum album*. The chief commercial varieties of oil of sandal-wood, in addition to the East Indian, are Macassar and West Australian. Other less important varieties are the West Indian and African oils. The East Indian and Macassar oils are derived from *Santalum album*, while the Australian variety is often the product of several plants; the oil known as Swan River oil being obtained from *S. cygnorum*.

Official oil of sandal-wood is a somewhat viscid, pale yellow oil, having a characteristic, strongly aromatic odour and a pungent and spicy taste. The British Pharmacopœia requires the oil to have a specific gravity between 0.975 and 0.980,[1] and to be soluble in six volumes of 70 per cent. alcohol (*U. S. P.*, soluble in 5 volumes). This latter test ensures the absence of cedarwood oil, and possibly other adulterants. The oil should have an optical rotation (according to the British and U. S. Pharmacopœias) of from —16° to —20° in a 100 mm. tube. These limits of optical activity are so arranged as to exclude any other variety of oil than the product of *S. album*.

The specific gravity of the official (East Indian) sandal-wood oil is usually slightly higher than the other oils of sandal-wood. E. J. Parry states that he has found genuine samples to range in specific gravity from 0.973 to 0.981. The higher limit of specific gravity of the British Pharmacopœia (0.980) might perhaps with advantage be raised to 0.985, as in the German Pharmacopœia. It has been pointed out that the gravity of sandal-wood oil continually increases from the commencement of the distillation to the end, so that it is necessary to take the distillation as far as possible. Thus Parry found that the density of the oil in the first, middle and last portions of the distillate was 0.965, 0.976, and 0.981 respectively.

Oil of sandal-wood varies to an appreciable extent according to the character of the wood used in distillation. Oils from billets and roots have the finest aroma and are most used in

[1] The 1885 edition of the British Pharmacopœia directed that sandalwood oil should have a specific gravity of about 0.960, but this inaccuracy was subsequently altered (1898) as shown in the text. The U. S. Pharmacopœia gives the limits of specific gravity as 0.965 to 0.975 at 25° C.

perfumery; while oils from chips contain most santalol and are the best for pharmaceutical use.

The pharmacopœial limits for optical rotation are rarely exceeded. All genuine oils give figures between —15° and —20°, and usually between —17° and —19°, in a 100 mm. tube. Most samples of genuine sandal-wood oil are soluble in 4 to 4.5 parts of 70 per cent. alcohol at 20° C.

Oil of sandal-wood distils (at ordinary atmospheric pressure) between 275° and 295° C., with decomposition. The results obtained by distillation under a reduced pressure of 14 mm. are much more valuable for the detection of adulteration. Sandal-wood oil thus distils between 155° and 170° C., while cedar-wood oil, a frequent adulterant of sandal-wood oil, distils largely below 150° C. under the same conditions. According to Parry and Bennett (*Chem. and Druggist*, 1904, p. 202) genuine oil of sandal-wood (East Indian) when distilled under this reduced pressure and the distillate collected in 10 per cent. fractions, gives the following results:—The specific gravity of the fractions varies from 0.964 to 0.988; the optical rotation from —14° to —22°; and the refractive-index from 1.5038 to 1.5123. No fraction should have a refractive-index below 1.5000, and the optical rotation of the fractions should vary only within narrow limits, when distilled as above. The refractive-index of eight genuine samples of sandal-wood oil was found by Parry and Bennett to vary from 1.5040 to 1.5075 (usually about 1.5060). This figure should never be below 1.5030.

The U. S. Pharmacopœia contains the following test for the detection of chloroform in adulterated oils:—Fold a small strip of filter-paper into the form of a taper, saturate it with sandal-wood oil, ignite the oil on the taper, and absorb the soluble portions of the products of combustion by holding over the flame an inverted beaker moistened on the inside with distilled water. The presence of a chloride in the water after the test is completed is evidence of the presence of chlorinated products (such as chloroform) in the original oil.

The composition of sandal-wood oil has for a long time been the subject of much research,[1] since the chemistry of the alcoholic bodies present (forming about 94 to 98 per cent. of the

[1] The following are some of the chief papers which have been published on this subject:—P. Chapoteaut, *Bull. Soc. Chim.*, 1882, xxxvii, p. 308; Chapman and Burgess, *Proc. Chem. Soc.*, 1896, xii, p. 140; E. J. Parry, *Chem. and Druggist*, lv, 1899, p. 1023; Schimmel & Co., *Semi-Annual Report*, 1899, April, p. 39; 1900, April, p. 43; M. Guerbet, *Compt. rend.*, cxxx, pp. 417 and 1324; absts. *Pharm. Journ.*, 1900, i, 496; A. C. Chapman, *J. C. S.*, 1901, lxxix, 134; M. Potvliet, *Brit. and Col. Druggist*, 1901, p. 173; Von Soden, and Soden and Müller, *Pharm. Zeit.*, xliv, p. 258; *Arch. Pharm.*, ccxxxviii, p. 359.

oil) was until recently in a very confused state. The subject is by no means fully cleared up, but it seems certain now that the so-called "santalol" is a mixture of *at least* two alcohols, (isomeric?) termed α- and β-santalols, of which the former is present in the larger quantity and is probably slightly dextro-rotatory, the latter being a strongly lævo-rotatory compound (about —45°). Many authorities doubt the accuracy of the formula $C_{15}H_{25}.OH$ for "santalol"; thus Schimmel & Co. consider that it is either a mixture of isomeric alcohols of the formula $C_{15}H_{21}.OH$, or consists of non-isomeric alcohols. Other formula have been suggested (*e. g.*, $C_{15}H_{24}O$) but the constituent alcohols have not yet been isolated in a pure state. It is possible that a third alcohol may be present in the "santalol" mixture.

In addition to the two or more alcohols ("santalol"), sandal-wood oil contains a small proportion of esters of these or other unidentified alcohols; santalal, $C_{15}H_{24}O$, 3 per cent.; α- and β-santalenes, 6 per cent. (b.pt., 253° and 263° C. respectively); traces of acetic and formic acids; teresantalic acid, $C_{10}H_{14}O_2$; santalic acid, $C_{15}H_{24}O_2$[1] (total acids about 3 per cent., mostly as esters); and, according to Müller, a compound, C_9H_{14} ("santene"), a lower homologue of the terpenes, and santalone, $C_{11}H_{16}O$ (isomeric with jasmone). The odorous substances (b.pt., 210° to 220° C.) of the oil have not yet been identified, unless the ketone santalone be one of them.

The acetylation process was first applied by E. J. Parry (*Pharm. Journ.*, lv, p. 118) to the examination of oil of sandal-wood. It is carried out as described on page 229. Pure oils require from 0.7 to 1.5 per cent. KOH for the saponification of the esters; but after acetylation the oil takes up 20 to 21 per cent. of KOH, owing to the presence of the large proportion of alcohols. Calculated as $C_{15}H_{26}O$, the proportion of alcoholic constituents should never fall below 90 per cent., and a standard somewhat higher than this, say 92.5 per cent., as suggested by M. Potvliet (*Brit. and Col. Druggist*, 1901, page 173), would be preferable. The U. S. Pharmacopœia (8th Rev.), in which this method of valuation is now adopted, requires at least 90 per cent. of alcohols as "santalol." The usefulness of the acetylation method as a means of detecting adulteration may be seen from the following figures given by various oils used as adulterants, in comparison with pure sandal-wood oil:—

[1] Oxidising agents, as for example potassium permanganate, act upon sandal-wood oil with the formation of a crystalline acid, termed by A. C. Chapman *santalenic acid*. It is possible that further investigations as to the constitution of this acid may throw some new light on the constitution of the sandal alcohols.

Oil, &c.	Alcohols by Acetylation. (Calculated as Santalol, $C_{15}H_{23}OH$.) (per cent.)
Sandal-wood East Indian,	92 to 98
" West Australian,	about 75
Cedar-wood,	8 to 12
Gurjun balsam,	7 to 10
Copaiba balsam,	5 to 8

The above-mentioned adulterants, together with castor oil, are those usually added to sandal-wood oil. The last-named adulterant may be identified by the lowered specific gravity of the sample, and by the high saponification number of the oil. E. J. Parry has recently recorded the adulteration of sandal-wood oil with the soluble fractions of West Indian oil together with terpineol, the latter compound serving to give a fictitious santalol-value. The specific gravity of these adulterated oils was slightly low, while the optical rotation was also decreased in some cases (—14°). (*Chem. and Druggist*, 1906, Feb. 3.)

The iodine absorptions of five samples of sandal-wood oil of undoubted purity were found by E. J. Parry to vary from 190.6 to 210.3. Higher results (up to 246) were obtained by Pearmain and Moor. Similar figures are given by cedar-wood oil and the method does not, therefore, appear to be of much value as a test of purity.

A large proportion of the sandal-wood oil used in medicine is put up in the form of capsules. The oil in these capsules is frequently grossly adulterated or is of an inferior quality. Many have been found to contain cedar-wood oil, or one of the non-official sandal-wood oils (*e. g.*, West Indian). E. J. Parry (*Chem. and Druggist*, 1906, p. 952) has called attention to the grossly adulterated capsules now on the market, many specimens consisting largely of West Indian oil. Since it is the "santalol" of these oils which is of medicinal value, the percentage of this mixture of constituents should always be determined. Further, it should be borne in mind that small quantities of West Indian sandal-wood and cedar-wood oils (about 4 per cent. of each) may be added to East Indian sandal-wood oil (see M. Potvliet, *Brit. and Col. Druggist*, 1901, p. 173) without any appreciable departure from the physical and chemical characters of genuine official sandal-wood oil.

West Australian Sandal-wood Oil is chiefly the product of *Santalum cygnorum*, although certain other trees are said to be employed to a small extent. The specific gravity of this oil is lower than that of the East Indian variety, being about 0.950 to 0.965 at 15° C. It is usually slightly dextro-rotatory, about +5°. E. J. Parry (*Chem. and Druggist*, 1898, liii, p. 708) has recorded the results of the analysis of four samples of this oil. They contained on the average 75.7 per cent. of "santalol"

(by acetylisation). Parry believes, however, that other reactions occur during the process, and hence the above figure probably does not represent the true amount of sesquiterpene alcohols present in the oils.

The iodine absorption of these four samples of West Australian oil was found by Parry to range from 197.6 to 204.5 per cent. The potash absorbed ranged from 1.15 to 1.66 per cent. The chief characters of the less important varieties of sandalwood oil are shown in the following table:—

Variety of Oil.	Botanical Source.	Specific Gravity at 15° C.	Optical Rotation in 100 mm. Tube.	Constituents and Characters.
West Indian, ...	*Amyris balsamifera (Schimmelia oleifera).*	.955 to .965	+25° to +30°	30 to 40 per cent. of alcohols, as "santalol," $C_{15}H_{26}O$; 16 per cent. cadinene and other sesquiterpenes.
African, ...	Unknown.	0.969	...	Similar to West Indian oil.
South Australian, ..	*Santalum preissianum.*	1.022	...	Solidifies on cooling; contains a solid alcoholic body, $C_{15}H_{24}O$, m.pt.,101–102°.
Fiji, ...	*S. yasi.*	.9768	—25.8°	...
Macassar, ...	*S. album.*	.974 to .976	—10.6° to —16.1°	Sol. in 5 to 6 parts 70 per cent. alcohol; 88 to 92.5 per cent. "santalol."

West Indian oil is characterised by its insolubility in 70 per cent. alcohol, most samples of the oil requiring over 80 parts for solution. As seen from the table, it is not a true sandalwood oil. Von Soden has isolated from this variety of oil a sesquiterpene alcohol (or mixture of isomeric alcohols), termed by him "amyrol," $C_{15}H_{26}O$. Amyrol boils at 299° to 301°, and is soluble in 3 to 3.5 parts of 70 per cent. alcohol at 20° C. A compound termed *amyrolin*, $C_{24}H_{12}O_3$, is also present (Von Soden and Rojahn, *Chem. Zeit.*, 1900, p. 349; abst. *J. C. S. I.*, 1901, xx, 64).

Snake-root Oils. Oils of Asarum Europæum and Asarum Canadense.

These two oils are the products of the distillation of the rhizomes and roots of *A. Europæum* and *A. Canadense* respectively. The chief known characters of the different snakeroot oils are contained in the following table:—

Oil.	Source.	Specific Gravity at 15.5.°	Other Characters and Constituents.
European snake-root.	Rhizome and root.	1.018 to 1.068	Brown colour and aromatic odour. On long standing, the oil is said to deposit crystals of asarone. Contains *lævo*-pinene; methyl-eugenol or -isoeugenol, and a blue-green high-boiling fraction.
Canadian snake-root.	Rhizome aud root.	0.930 to 0.960	Yellow or yellowish-brown oil of strong aromatic odour. Optical rotation, —3.5° for 100 mm. Contains *d*- and *l*-pinenes (2 per cent.); *d*-linalol; *d*-borneol; *l*-terpineol; geraniol (total alcohols, 35 per cent.); methyl-eugenol (37 per cent.); a phenol, $C_9H_{12}O_2$; a lactone, $C_{14}H_{20}O_2$; *a mixture of fatty acids, including* acetic and palmitic; a blue oil, consisting of *oxygenated bodies of* an alcoholic nature (about 20 per cent.).
Virginian snake-root.	Whole herb of *Aristolochia serpentaria.*	0.980 to 0.990	Contains borneol.
...	Root of *A. reticulata.*	0.974 to 0.978	Optical rotation, = —4°; contains pinene and borneol.
...	Root of *A. clematis.*	About 0.910	A thick yellow oil.
...	Dried herb of *Asarum arifolium.*	1.0585 to 1.0613	Optical rotation, —2.5° to —3.7°. Contains safrol (chief constituent); *lævo*-pinene; eugenol; a phenol; methyl-eugenol and methyl-iso-eugenol; asarone, and a sesquiterpene.

It would appear that a further investigation of the composition of some of these oils is desirable, although they are not of any great importance. Our present knowledge of them, as given in the above table, is chiefly due to the researches of F. B. Power (*Proc. Amer. Pharm. Assoc.*, 1880, xxviii, p. 464); Petersen (*Arch. Pharm.*, ccxxvi, p. 123) and Power and Lees (*Jour. Chem. Soc.*, 1902, p. 59).

Thyme Oil.

This oil is obtained by the distillation of *Thymus vulgaris*, and is produced largely in Spain and France. The Spanish oil is the more valuable. In the south of France the oil not infrequently suffers admixture with the oil of *Thymus serpyllum*, and with French oil of turpentine.

Two varieties of oil of thyme, namely the "red" and "white," are known in commerce. The unrectified ("red") oil is stated to owe its colour to the action of the phenolic constituents of the oil on the iron of the apparatus employed in the distillation. The oil can be rectified to a light yellow-coloured oil ("white

oil of thyme"). The specific gravity of thyme oil ranges from about 0.905 to 0.935. It is slightly lævo-rotatory, to —3° for 100 mm. Thyme oil is soluble in half its measure of 90 per cent. alcohol, in 1 to 2 measures of 80 per cent., whilst with from 15 to 30 measures of 70 per cent. alcohol most genuine thyme oils afford a clear solution.

The constituents of thyme oil, so far as known, are the phenols thymol and carvacrol;[1] the alcohols linalol and borneol; bornyl acetate; menthene (15 per cent.); cymene, and (possibly) lævo-pinene.[2]

The phenolic constituents of thyme oil are perhaps the most important, although there is no doubt that the borneol and linalol contribute to the odour of the oil. The percentage of thymol and carvacrol in thyme oil is usually about 20 to 30, *and should never fall below 20. The phenols may be determined approximately by noting the proportion dissolved out by caustic* soda solution,[3] or by observing the amount of distillate obtained above 220° C. This should not be less than 25 per cent. of the oil.

The following method for the determination of the phenols in thyme oil is due to Kremers and Schreiner[4] (*Pharm. Review*, 1896, p. 221; abst. *Jour. Soc. Chem. Ind.*, 1897, p. 568):—

Five cc. of the oil to be examined is weighed and introduced into a burette. The oil is diluted with about an equal volume of petroleum-ether, when a 5 per cent. solution of potassium hydroxide is added and the mixture vigorously shaken for a short time. The liquid is then allowed to stand until separation is complete. The alkaline solution is now run off into a 100 cc. flask. The agitation with the caustic potash is repeated until no further diminution of the volume of the oil occurs.

The alkaline liquid containing the dissolved thymol is now

[1] Thymol and carvacrol do not appear to be constantly present together in thyme oil. The conditions under which one or other of these isomeric phenols is present are not definitely known. Schimmel & Co. found that the oil from dried French thyme contained much thymol but only a little carvacrol. Fresh and dry thyme (German) gave oils containing only thymol. Spanish thyme oil was found to contain carvacrol and no thymol.

[2] H. Labbé (*Bull. Soc. Chim.*, 1898, xix, p. 1009) could not obtain any evidence of the presence of pinene in this oil, although he isolated a hydrocarbon boiling at 156° to 158° C., which gave a nitroso-chloride melting at 106.5°. Labbé suggests that the oil examined by Schimmel & Co. and found to contain pinene was adulterated with oil of turpentine.

[3] The U. S. Pharmacopœia (8th Rev.) requires thyme oil to contain at least 20 per cent. by volume of phenols, the oil being assayed by shaking 10 cc. of the sample in a corked burette with 20 cc. of 5 per cent. caustic soda solution, and setting the mixture aside for 12 to 24 hours. The volume of unabsorbed (non-phenol) oil is then noted, and the proportion of phenols deduced.

[4] *The method is in reality a modification of that of* Messinger and Vortmann (*Ber.*, 1890, xxiii, p. 2753; see p. 74).

made up to a definite volume (100 or 200 cc.) with 5 per cent. caustic potash solution. An aliquot portion of this liquid (say 10 cc.) is now introduced into a 500 cc. flask, and decinormal iodine solution added in slight excess.[1] The thymol combines with the iodine, and a reddish-brown precipitate is produced. When excess of iodine has been added, the liquid is rendered slightly acid with dilute hydrochloric acid, and diluted to 500 cc. with water. One-fifth of the liquid (100 cc.) is now filtered off, and titrated with decinormal sodium thiosulphate solution. Each cc. of decinormal iodine solution is equivalent to 0.003741 gramme of thymol, the reaction which occurs being represented by the following equation:—

$$\underset{\text{Thymol.}}{C_{10}H_{14}O} + 2I_2 + 2NaOH = \underset{\text{Di-iodo-thymol.}}{C_{10}H_{12}I_2O} + 2NaI + 2H_2O.$$

In the case of carvacrol, a finely divided white precipitate is produced with the iodine solution. The liquid is therefore vigorously shaken after the addition of the iodine solution and then filtered. The filtrate is next acidulated with hydrochloric acid, and the process continued exactly as the determination of thymol. Since thymol and carvacrol are isomeric methyl-propyl phenols, and the same reaction occurs in both cases, the calculation in the case of the latter is the same as for thymol.

"White" French thyme oil is said to be almost invariably of poor quality, and as has been stated, is frequently adulterated with French oil of turpentine. Such adulterated oils would be strongly lævo-rotatory. The addition of the oil from *Thymus serpyllum* (wild thyme) to genuine thyme oil also increases the rotation (see table on next page).

The abstraction of thymol from thyme oil is much practised, and it is therefore important to determine, at least approximately, the proportion of phenols present in the oil, as described on page 473. On the other hand, the phenols are not the only constituents contributing to the odour of thyme oil, since linalol and borneol are present to the extent of about 5 and 8 per cent. respectively. Thyme oils which have suffered abstraction of the greater part of their thymol frequently possess a very fair odour. The addition of *phenol* to thyme oil may be detected by agitating the oil with a little *hot* water, when no blue or violet colour should be produced in the aqueous liquid on the addition of ferric chloride solution (*U. S. Pharmacopœia*).

[1] In order to determine whether an excess of iodine has been added, a few drops of the liquid in a test-tube should be treated with a little dilute hydrochloric acid. If insufficient iodine has been added, the liquid will become milky owing to the separation of thymol. In the presence of an excess of iodine, a brown colour only will be seen.

The less important varieties of thyme oil are described in the following table:—

Oil.	Botanical Source. Root of:	Specific Gravity.	Optical Rotation °.	Characters and Constituents.
Wild thyme.	*Thymus serpyllum.*	0.890 to 0.920	—10° to —21°	Cymene; a sesquiterpene; one or more phenols.
...	*T. capitatus.*			
...	*T. camphoratus.*	About 0.900	...	Pinene; cymene; dipentene; thymol (?); carvacrol (?); bornyl acetate.

Turpentine Oil.[1] Spirit of Turpentine.[2]

Oil of turpentine is contained in the wood, bark, leaves, and other parts of pines, firs, and other coniferous trees, and is usually prepared by distilling, either with water or alone, the crude turpentine or oleo-resinous juice which exudes from incisions in the bark of the trees. The non-volatile portion constitutes *rosin* or *colophony* (page 157), and the distillate, varying in yield from 10 to 25 per cent., is the volatile oil or spirit of turpentine, vulgarly known as "turps." *Rectified oil of turpentine* is obtained by treating the first product with alkali, to saturate any resin acids, and redistilling, preferably in a current of steam.

The principal varieties of oil of turpentine met with in commerce in the United Kingdom are the American and Russian. The so-called English or English-distilled turpentine oil is either American or Russian oil imported into or distilled in Great Britain, or a substitute derived from petroleum and mixed with more or less genuine oil of turpentine. French turpentine oil is difficult to obtain and has ceased to be an article of ordinary commerce in Great Britain. Though presenting close resemblances, these varieties are not strictly identical, as will be evident from the following description:—

French turpentine oil is manufactured chiefly from the crude turpentine or "gum" yielded by the *Pinus maritima*, but smaller quantities are obtained from the *pin franc*, or frankincense pine. Of late years, the distillation has been conducted by blowing superheated steam into the still containing the gum, no external heat being employed. To this improved mode of manufacture the very constant character of the product is probably due. French oil of turpentine after neutralisation and rectification consists almost entirely of *lævo-pinene* or terebentene, which has already been fully described (page 262). Smaller proportions

[1] The author and editor are indebted to L. Archbutt for perusal and criticism of this article.

[2] French, *Essence de Térébentine;* German, *Terpentinöl.*

of other terpenes, of cymene, and of *resinous matters*, are also present in the commercial oil.

American turpentine oil is obtained from the turpentine collected in North Carolina and other Southern States of the American Union, from various species of pine.[1] Its main constituent is *dextro-pinene* or australene, having the same boiling-point, specific gravity, and chemical characters as the terebentene of the French oil, but differing from that body in being usually *dextro*-rotatory. With this exception, and the fact that French oil of turpentine appears to absorb oxygen somewhat less rapidly than the American product, the characters of the two oils are practically identical.

Russian oil of turpentine is chiefly the product of *Pinus sylvestris*,[2] but *P. Ledebourii* and other species also contribute to it. A sample of Russian turpentine oil, of 0.8682 specific gravity, examined by W. A. Tilden, was found to contain from 10 to 15 per cent. of a pinene boiling at about the same temperature as australene, but having the specific rotation of +23.5°; 65 to 70 per cent. of sylvestrene; a considerable quantity of cymene; and small proportions of viscid hydrocarbons boiling at high temperatures. But Russian oil of turpentine is very variable in character, the normal constituents being accompanied with more or less of the products of the destructive distillation both of the rosin and the wood, including benzenoid hydrocarbons, phenoloid bodies, furfurane or tetrol ($C_4H_3.OH$), and sylvane (methyl-tetrol, $C_4H_3.OCH_3$), &c.

The specific gravity of the Russian oil of commerce varies from 0.8620 to 0.8722, and it contains matters not volatile at 100°, in proportions ranging from 0.5 to 2.4 grammes per 100 cc. (C. T. Kingzett, *J. S. C. I.*, v, p. 10). Russian oil of turpentine has a characteristic odour, which is quite distinct from that of American or French origin. It is not generally used in the man-

[1] According to J. H. Long, the greater part of American turpentine oil is obtained from the long-leaf pine (*Pinus Australis*). The "loblolly" or "oldfield" pine (*P. tæda*), the "pitch" pine (*P. rigida*), and the "swamp" or Cuban pine (*P. Cubensis*) supply comparatively small quantities only. The crude turpentine is collected in pockets cut in the trees a few feet from the ground. The distillation of the product is conducted in copper retorts, water being added so that the oil may pass over in a current of steam. The vapor is condensed in a worm surrounded with cold water, and the liquid flows into a tank, the oil collecting on the surface. A bowl of crude turpentine or "gum" weighs about 280 lbs. and yields from 7 to 9 gallons of the oil; the weight of the rosin remaining in the still being about four times that of the oil obtained. The American production of turpentine oil is stated to be about 300,000 barrels annually, of which more than half is exported, chiefly from Savannah, Georgia, and Wilmington, North Carolina.

[2] The Russian turpentine oil of commerce is a very different product from that obtained by distilling young leaves and cones of *Pinus sylvestris* with water (see J. C. Umney, *Pharm. Journ.*, 1895, ii, 542).

ufacture of paint, though there does not appear to be any good reason against the use of the refined Russian oil for this purpose. The oil finds a special application, under the name of "tar spirits," as a solvent of cotton-seed oil pitch for the manufacture of tar-varnishes.[1]

The great readiness with which Russian turpentine oil absorbs oxygen and becomes viscid specially adapts it for the manufacture of the disinfectant known as *Sanitas*.

Swedish oil of turpentine is obtained from sources identical with the Russian product, which it closely resembles. A sample of so-called Swedish oil examined by L. Archbutt several years ago was a substitute, containing not more than 10 per cent. of real oil of turpentine.

Finland Turpentine Oil.—The following results of the examination of three samples of turpentine oil from Finland have been published by Aschan and Hjelt (*Chem. Zeit.*, 1894, xviii, p. 1566; *Jour. Soc. Chem. Ind.*, 1895, p. 169). The oil is obtained from the trunks and roots of *Pinus sylvestris* and *P. abies*, the distillation being conducted at a high temperature. The crude oil is freed from acetic acid and tarry matters by distillation over lime.

Oil from South Finland.—Fractional distillation yielded 7.1 per cent. boiling at from 155° to 160° C.; 30.2 per cent. boiling at from 160° to 165° C.; 22.6 per cent. boiling at from 165° to 170° C.; and 20.1 per cent. boiling at from 170° to 175° C. The first fraction consists chiefly of pinene, the higher fractions chiefly of sylvestrene and dipentene. This turpentine oil is therefore identical in composition with Swedish and Russian oils.

Oil from North Finland.—The bulk of this oil distils at between 170° and 178° C. The lower boiling portions consist chiefly of pinene, but the larger proportion of the oil consists of dipentene with scarcely any sylvestrene.

Turpentine obtained by distilling resinous wood with steam.—The chief fraction distils between 155° and 160° C., and contains much pinene. In the higher fractions sylvestrene, but no dipentene, was observed. From this it is concluded that whilst sylvestrene occurs ready-formed in the resin of the northern coniferous trees, dipentene is not a natural product, but is formed by the superheating of the pinene during the process of distillation.

While exhibiting more or less characteristic differences in certain respects (*e. g.*, optical activity, boiling-point), oils of turpentine from different sources present a close general similarity, and the following description, though applicable in particu-

[1] *Tar varnishes* are employed largely for varnishing iron bedsteads, umbrella ribs, cycle frames, &c., which are stoved after being painted, and the Russian oil is said to have less tendency than the American product to "kill the gloss."

lar to oils of American origin, may be accepted as generally accurate:—

Commercial oil of turpentine has a peculiar characteristic odour and a pungent taste.[1] The specific gravity ranges from 0.862 to 0.875. French and American oils begin to boil between 156° and 160° C., and fully 90 per cent. usually distils below 173° C. Russian oil distils at a higher temperature, the greater part passing over between 165° and 190° C. Old samples of turpentine oil leave a small proportion of non-volatile resinous matter on distillation.

Oil of turpentine is readily combustible and burns with a very smoky flame.

Oil of turpentine is almost wholly insoluble in water, glycerin, and dilute alkaline and acid solutions. It is very soluble in absolute alcohol, but its solubility is greatly reduced by the presence of water, spirit of 0.850 specific gravity dissolving only 10 per cent. of its weight of oil of turpentine.

Oil of turpentine is very soluble in (probably miscible in all proportions with) ether, carbon disulphide, chloroform, benzene, petroleum-spirit, and fixed and essential oils.

Oil of turpentine is itself a solvent for sulphur, phosphorus, resins, fats, waxes, caoutchouc, &c. The oil has been used as an antidote for phosphorus-poisoning, a compound containing $C_{10}H_{15}.(OH)_2.P:O$ and melting at 85° C. being stated to be formed.

For pharmaceutical purposes, oil of turpentine should be purified by agitation with milk of lime and then distilled in a current of steam.[2]

[1] According to H. Schiff (*Chem. Zeit.*, xx, 361) the odour commonly associated with oil of turpentine is due to the presence of a small proportion (under 1 per cent.) of an aldehydic oxidation-product, probably of the formula $C_{10}H_{16}O_3$, which is formed when the oil is exposed to a feeble light in an imperfectly closed vessel. On treating the oil with sodium bisulphite solution this aldehydic body is removed, and the purified oil retains only a slight ethereal aroma; but the characteristic odour soon returns if the oil is exposed to the air. It is a noteworthy fact that the odours of American, French, and Russian turpentine oils are quite distinct.

[2] E. Kremers (*Pharm. Rev.*, 1897, xv, 7) has recorded the following figures yielded by a sample of crude oil of turpentine when subjected to the above process of purification. One litre of the crude oil of sp. gr. 0.872 at 20° C., and rotatory power $[\alpha]_D = +11.616°$ was agitated with an equal volume of milk of lime, and after an interval of at least 12 hours, distilled in a current of steam, 4 fractions of 200 cc. each being collected, and the residual 200 cc. rejected:—

Fraction.	Sp. Gr. at 20° C.	$[\alpha]_D$.
1	0.864	+14.180
2	0.866	+12.297
3	0.8702	+11.429
4	0.8722	+10.700

The decrease in volatility was, therefore, accompanied by a diminution of rotatory power, as has been noticed by others. In another similar

Oil of turpentine, even when clear, is practically never wholly free from water. On distillation, the first fractions are usually turbid owing to the presence of water. The facile formation of hydrogen peroxide in presence of turpentine oil and its subsequent decomposition into oxygen and water, may account for this fact. Petroleum spirit does not contain appreciable traces of water.

Turpentine oil absorbs oxygen on exposure to air, gradually becoming viscid and ultimately resinous. It is this property which gives turpentine oil its peculiar value—not shared by its substitutes—to the painter and varnish-maker, since the turpentine acts as an oxygen-carrier to the drying oil, and the resin formed acts as a binding material for the pigments with which it is mixed. C. T. Kingzett,[1] who has studied the reaction very fully, finds that the oxidation of turpentine oil, whether in presence or absence of water, results in the formation of an organic peroxide which is held in solution in the oxidised oil. This so-called *camphoric peroxide*, which does not appear to have been isolated, suffers chemical change by contact with water with formation of hydrogen peroxide. Hence, when the oxidation is effected in the presence of water, hydrogen peroxide is always found in the aqueous liquid, together with at least two other compounds, one of which has a composition corresponding to the formula $C_{10}H_{16}O_3$, and yields cymene on distillation with dilute sulphuric acid; while the other resembles thymol in composition and some properties, but so far has been obtained only as an oily body. Kingzett believes that in the limited oxidation of turpentine oil and other essential oils by air the terpene grouping is not broken down, as no product which can be assumed to contain less than C_{10} is obtained from pure oils. The disinfectant introduced by Kingzett under the name of *Sanitas* is produced by passing air through Russian oil of turpentine in contact with warm water.

On leaving turpentine oil in contact with water, it is gradually converted into *terpin hydrate* (page 347).

Chlorine and bromine combine with oil of turpentine with such energy that inflammation frequently occurs, with separation of carbon. When dissolved in carbon tetrachloride or chloroform, turpentine oil absorbs very nearly two molecules of bromine ($2Br_2$). Iodine is dissolved by turpentine oil to form a green solution, which ultimately becomes hot and gives off hydriodic acid; and

experiment the whole (mixed) distillate was dried over anhydrous sodium sulphate. The oil possessed an agreeable odour, its sp. gr. was 0.864 at 20° C. and specific rotation +12.177°. Rectification over milk of lime, in the manner described, results, therefore, in the production of an oil of excellent quality.

[1] *Proc. Chem. Soc.*, 1894, p. 51. Further studies on the Kingzett reaction will be found in *Berichte*, 1898, xxxi, 3046, and *Jour. Soc. Chem. Ind.*, 1897, p. 832.

when considerable quantities of iodine and turpentine oil are suddenly brought together, explosion frequently ensues. When distilled with bleaching powder and water, turpentine oil yields a considerable proportion of chloroform.

Moderately strong nitric acid oxidises turpentine oil to resinous bodies, which ultimately yield terebic acid, $C_7H_{10}O_4$,[1] terpenylic acid, $C_8H_{12}O_4$,[1] oxalic acid, acetic acid, and other products. Ordinary turpentine oil yields terephthalic and paratoluic acids in addition, but these products are chiefly due to the oxidation of the cymene present, and are formed in traces only by the oxidation of pure pinene. Fuming nitric acid acts very violently on oil of turpentine, often setting it on fire.

Strong chromic acid mixture oxidises turpentine oil chiefly to acetic acid, but a weaker reagent produces terpenylic acid. If cymene be present, terephthalic acid (page 128) appears amongst the products of the oxidation.

Further information respecting the chemistry of oil of turpentine is given on page 496.

While presenting close resemblances in most respects, the oils of turpentine from different sources exhibit differences which are more or less characteristic, in their optical activities, as shown in the following table. The figures show the optical rotation of the oils for the sodium ray for a thickness of 100 millimetres.[2]

Source.	Optical Rotation °.	Number of Samples.	Authority.
French—			
Pure terebentene (*l*-pinene),	—40.4	...	W. A. Tilden.
Commercial oil,	—30 to —30.5	...	H. E. Armstrong.
Commercial oil,	—25.3	...	C. Symes.
American—			
Pure australene (*d*-pinene),	+21.5	...	W. A. Tilden.
Oil shipped at Wilmington,	+12.3 to +16.3	35	H. E. Armstrong.
Oil shipped at Savannah,	+ 8.8 to +12.0	12	"
Oil shipped at Charleston,	+ 9.5 to +16.7	9	"
Commercial samples,	+12 to +15.3	...	A. Wilson.
Oil from Columbia, S. C.,	— 2 to +18.9	6	J. H. Long.
Oil from Wilmington, N. C.,	+ 8.3 to +19.8	5	"
Oil from Mobile, Ala.,	—34.8 to +29.6	13	"
Commercial samples,	+ 9.7 to +16.9	13	"
Commercial samples,	+ 7.6 to +15.9	11	L. Archbutt.
Russian—			
Pure sylvestrene,	+19.6	...	W. A. Tilden.
Commercial oil,	+15 to +23.4	23	H. E. Armstrong.
Commercial oil,	+15 to +22.2	67	C. T. Kingzett.

[1] See a paper by W. T. Laurence on the synthesis and preparation of terebic and terpenylic acids, *Jour. Chem. Soc.*, 1899, lxxv, 527.

[2] Instruments intended for observing the angular rotation for the transition tint are not suitable for examining the optical activity of turpentine oil.

The oil shipped from Charleston comprises turpentine of somewhat high dextro-rotatory power, as well as oil of the Wilmington and Savannah types. Other American ports furnish a somewhat irregular product; but the values always lie between the extremes given in the table, and in the majority of cases the oils belong to the Wilmington type, Brunswick alone exhibiting a marked tendency to furnish a product of the Savannah type (H. E. Armstrong, *J. S. C. I.*, 1882, p. 478).

ADULTERATIONS OF TURPENTINE OIL.—The most usual adulterants of oil of turpentine are certain fractions of petroleum known as "turpentine substitute," and "rosin spirit," which is the more volatile portion of the product obtained by distilling ordinary rosin. Certain fractions of shale oil and coal tar are not improbable adulterants, but their employment is not common. The table on the next page gives a number of distinctions between real turpentine oil and its substitutes.

The *index of refraction* of turpentine oil is a useful indication of its purity, especially in confirmation of other tests. Genuine oil of turpentine was found by T. Macfarlane (*Canadian Inland Revenue Department, 1901, Bulletin No.* 79) to have a refractive index ranging from 1.4667 to 1.4722 at 20° C.[1] Rosin spirit ("spiritine") has a similar refractive-index, while light petroleum products and coal oil have lower refractive-indices than oil of turpentine (see table, page 482).

The observation of the *optical activity* of a sample of turpentine oil often affords valuable information as to its origin and general character. While the various adulterants of turpentine derived from shale and petroleum are always optically inactive, and those from rosin very frequently so, oil of turpentine always exhibits more or less rotation; but the optical activity of genuine samples, even when derived from the same locality (page 480), is so variable as to give the figures for the optical rotation but little quantitative value.

The *specific gravity* of turpentine oil given in the table on p. 482 includes the widest range observed in genuine commercial samples.[2] In the case of genuine samples, an exceptionally high gravity is due to the presence of oxidation products. The specific gravity increases rapidly on keeping unless precautions are taken to exclude air and light. T. Macfarlane (*Canadian Inland Revenue Department, 1901, Bulletin No.* 79) found the average

[1] Macfarlane's determinations were made at the temperature of the laboratory, and were corrected to 20° C. by the addition or subtraction of 0.0005 for each 1° C. above or below this temperature. The instrument was an Abbé-Zeiss refractometer, and was adjusted to read 1.3330 for water at 20° C.

[2] R. G. Dunwody found a number of samples of *commercial oil of turpentine* to vary in specific gravity from 0.856 to 0.876 before rectification, and from 0.851 to 0.873 after rectification.

CHARACTERS OF TURPENTINE OIL AND SUBSTITUTES.

	Turpentine Oil.	Robin-Spirit.	Petroleum-Naphtha.	Shale-Naphtha.	Coal-Tar Solvent Naphtha.
1. Index of refraction,	1.4667 to 1.4722	1.4701	1.4068	...	1.4341
2. Optical activity,	Active.	Variable.	None.	None.	None.
3. Specific gravity,	0.862 to 0.875	0.856 to 0.880	0.700 to 0.740	0.700 to 0.740	0.860 to 0.875
4. Temperature of distillation; ° C.	156 to 180	Gradual rise.	Gradual rise.	Gradual rise.	Gradual rise.
5. Action in the cold on coal-tar pitch (see vol. II, pt. ii, p. 99),	Readily dissolves pitch to a deep brown solution.	Readily dissolves pitch to a deep brown solution.	Very slight action.	Very slight action.	Readily dissolves pitch to a deep brown solution.
6. Behaviour with absolute phenol at 20° C. (see vol. II, pt. ii, p. 99),	Homogeneous mixture.	Homogeneous mixture.	No apparent solution.	Homogeneous mixture crystallising on cooling.	Homogeneous mixture.
7. Behaviour on agitating 3 measures of the cold sample with one measure of castor oil,	Homogeneous mixture.	Homogeneous mixture.	Liquid separates into two layers of nearly equal volume.	Behaves like petroleum naphtha.	...
8. Bromine absorption, dry,	203 to 236	184 to 203	10 to 20	60 to 80	...
9. Behaviour with sulphuric acid,	Almost completely polymerised.	Polymerised.	Very little action.	Considerable action.	Moderate action.

increase of a number of samples of oil of turpentine to amount to 3.4 per cent. of their weight. The increase for different samples was very variable. Rosin oil and light petroleum products do not appreciably increase in density on keeping.

Somewhat sharper figures characterise the gravity of turpentine oils from different sources. Thus:—

Range of Gravity at 15.5° C.	Kind of Oil.	Number of Samples.	Observer.	Reference.
0.8650 to 0.8695	American.	20	A. Wilson.	*Chem. Trade Jour.*, vi, 316.
0.8622 to 0.8655	American, distilled in laboratory.	13	J. H. Long.	*Chem. Trade Jour.*, x, 261.
0.8656 to 0.8748	American (commercial samples).	...	J. H. Long.	*Chem. Trade Jour.*, x, 261.
0.8615 to 0.8706	American.	157	L. Archbutt.	Communicated.
0.8617 to 0.8696	Russian.	8	L. Archbutt.	Communicated.

The specific gravity is in itself sufficient to indicate the presence of any considerable proportion of some adulterants of turpentine oil, but it is not of much value for quantitative purposes, owing to the variable character of the shale and petroleum products. In fact, heavier fractions of shale oil and petroleum are apt to be added to turpentine oil, although their presence is still more objectionable than the naphthas.

J. H. Long (*Chem. Trade Jour.*, x, 261) has suggested the determination of the vapour density of turpentine oil as a method for its technical examination. A specimen of the pure oil was distilled, and about 0.150 gramme of the fraction passing over between 155.5° and 156.5° C. examined by the V. and C. Meyer method (*Ber.*, 1878, p. 2253), ethyl benzoate being used as the heating liquid. Two experiments showed a vapour density of 4.68 and 4.66, corresponding to molecular weights of 135.1 and 134.5. Unfractionated commercial turpentine oil showed vapour densities ranging from 4.73 to 5.11. Samples of light petroleum products naturally gave lower figures.

The behaviour of turpentine oil with coal-tar pitch, phenol, and castor oil affords simple and useful tests for its purity; but the indications must be accepted with caution as the tests fail to detect certain adulterants even when present in considerable proportion. Thus R. G. Dunwody has pointed out (*Amer. Jour. Pharm.*, 1890, June) that a sample consisting of 35 per cent. of turpentine oil with 65 per cent. of petroleum-spirit will give a homogeneous mixture with castor oil. He states that both petroleum-spirit and turpentine oil are perfectly miscible with pure *glacial acetic acid*, but that a fairly sharp distinction between

them is obtainable by using glacial acetic acid containing 1 per cent. of water, since oil of turpentine is miscible with an equal measure of 99 per cent. glacial acetic acid, whereas petroleum is not.[1] Dunwody gives the following figures which, however, require verification with other samples of petroleum and turpentine oil:—

Petroleum,	1	2	3	4	5	7	8 cc.
Oil of turpentine,	9	8	7	6	5	3	2 cc.
Measure of acetic acid containing 1% of water required for solution,	40	60	80	110	150	230	270 cc.

Squire and Caines (*Pharm. Journ.*, 1902, 512) found that some samples of turpentine oil gave clear solutions with 99 per cent. acetic acid, but that others gave turbid solutions. Pure glacial acetic acid always gave clear solutions. The British Pharmacopœia (1898) states that oil of turpentine is soluble in its own volume of glacial acetic acid. According to W. Duncan, however (*Chemist and Druggist*, 1901, lviii, 474), many genuine samples require up to 5 parts of acetic acid for complete solution, and the test cannot therefore be relied upon as conclusive evidence of adulteration. Rosin oil and rosin spirit are both readily miscible with glacial acetic acid.

B. Redwood has pointed out that the presence of petroleum-spirit in turpentine oil is readily and certainly indicated by the reduced flash-point of the sample. Thus, while genuine American turpentine oil flashes at 92° F., the addition of as little as 1 per cent. of ordinary petroleum spirit lowers the flash-point by about 10° F. This statement has been traversed by E. J. Parry, who finds that the flash-point of genuine turpentine oil, as determined by Abel's close-test apparatus, varies from 92° to 98.5° F. In L. Archbutt's experience genuine oil of turpentine flashes at 90° F.

J. H. Long, in a valuable paper (*Chem. Trade Jour.*, x, 261), has given the flash-points and densities of mixtures of 95 per cent. of American turpentine oil, flashing at 32° C. (=89.6° F.), with 5 per cent. of such petroleum products as could be used for the sophistication of turpentine oil. The flash-point of a mixture is naturally reduced by the presence of the more volatile products, but is actually raised by the oils of higher density. The specific gravity of any mixture can be calculated from those of its components. Long also gives the following figures for the specific gravities and distillation temperatures of various petroleum products. By the term "initial temperature" of dis-

[1] P. H. Conradson (*Jour. Soc. Chem. Ind.*, 1890, p. 1005) has described a method applying glacial acetic acid to the residue obtained by evaporating 50 cc. of the sample of turpentine oil to 1 to 2 cc. on a water-bath. The process can have no claim to accuracy, and its practical value is not apparent.

tillation Long means the point at which about 1 cc. of the 100 cc. employed will have passed over:—

Product.	Specific Gravity.	Distillation Temperature. °C.	
		Initial.	Final.
Gasolene, ... 88° Baumé ...	.6508	About 40°	About 110°
Gasolene, ... 74° " ...	.7001	" 55°	" 125°
Benzine, ... 63° " ...	.7306	" 95°	" 165°
"Standard White," 110° fire test ...	.7999	" 130°	Above 360°
"Water White," .... 150° " ...	.7918	" 140°	About 310°
"Headlight," .... 175° " ...	.7952	" 160°	" 315°
Mineral seal oil, ...	.8293	" 230°	Above 360°
Paraffin oil, ...	.8906	" 300°	" 360°
Oil of turpentine, ...	.8680	" 156°	About 185°

It will be noted that the observed rotations of commercial oils of turpentine differ considerably from the specific rotatory powers of the terpenes said to form their chief constituents. J. H. Long has pointed out that the optical activity of commercial oil of turpentine of American origin is far more variable than is commonly assumed. Thus, while the great majority of specimens of American oil exhibit a marked dextro-rotation, samples are occasionally met with which are only feebly dextro-rotatory or which even exhibit lævo-rotation. In two cases the dextro-rotation reached 29.6 and 25.1° respectively, an activity which is greater than that attributed by Tilden to pure australene. Out of forty samples examined by Long (some of which were American oils of commerce and others prepared by him in the laboratory by distilling the fresh oleo-resins in copper with water) three samples exhibited lævo-rotation (—2.02°, —34.83°, and —16.92°). Long finds the oil from the *spruce-pine* (*Pinus glabra*) to be strongly lævo-rotatory, the angular rotation in a 2-decimetre tube ranging from about —63° to over —70°. On fractionally distilling the oil, the portions first passing over showed an angular rotation of —69° to —73° (for 200 mm.), which fell in the fractions of higher boiling-point to about 10° less. Long has further shown that the rotation of the fractions of oil of turpentine frequently becomes less and less in the higher fractions. In one case the optical rotation fell to +2°, while another sample gave on distillation a first fraction which had a rotation of —16.8 and a twelfth fraction having a rotation of —4.4°.

Long suggests that the lævo-rotation sometimes exhibited by American turpentine oil may be due to products from spruce-pines, especially from trees in the district around Mobile. He points out that in numerous oils known to be free from spruce a marked dextro-rotation was always observed, while low dextro-rotation was limited to oils distilled in districts where the

spruce-pine is occasionally found. Long affirms that turpentine from the same tree contains lævo- and dextro-pinene in varying proportions (*J. A. C. S.*, 1899, xxi, 639). The observation of Marsh and Gardner (*Jour. Chem. Soc.*, 1891, lix, 725) that the first fractions obtained by the distillation of turpentine oil have a greater optical activity than those of higher boiling-point, is confirmed by Long. In one case, the last fraction was *lævo-rotatory*, a fact which Long suggests may have been due to the presence of the hitherto unknown *lævo-cymene*.

Exposure to light or to air has been observed to increase the optical activity of turpentine oil.[1]

Fractional distillation, if carefully conducted, probably affords more information as to the origin and purity of oil of turpentine than any other single test, and if the optical activity of the fractions be also observed a further useful light will be thrown on the nature of the sample. Genuine American oil of turpentine commences to boil at 156° C., or within a degree or so of that temperature, the greater part passing over before the thermometer rises above 162°. As a rule, 90 per cent. or more passes over before the thermometer rises above 173°, and the distillation should be practically complete below 185°. Russian turpentine oil distils chiefly between 165° and 190°. On the other hand, petroleum, shale, and resin products commence to distil at very varying temperatures, according to their quality, but during the distillation the thermometer rises regularly through a considerable range.

The exact behaviour of a sample of turpentine oil on distillation depends materially on the precise manner in which the operation is conducted, and in any series of experiments, the results of which are meant to be comparable, the same conditions should be rigidly observed. Of course, the most perfect separation of the constituents is obtained by the use of a dephlegmator; but, for ordinary purposes, the distillation of the turpentine oil in a retort heated over a naked flame, with the thermometer bulb immersed in the liquid, will be found very satisfactory. The distillation should be conducted exactly in the manner described in Part II for the assay of commercial benzols.

The following table shows the behaviour of samples of genuine American oil of turpentine when fractionally distilled in the

[1] By submitting American oil of turpentine to fractional distillation, Armstrong obtained a portion having a specific rotation of +24.8°, and by submitting the original oil to air-oxidation and subsequently distilling off the unaltered hydrocarbon in a current of steam he several times obtained products of considerably higher rotatory power than the original oils. Similarly, the hydrocarbons carried over by the air current during the oxidation of Russian turpentine oil are almost free from sylvestrene and usually exhibit a higher rotatory power than the original crude turpentine from which they are derived.

author's laboratory, without dephlegmator, the thermometer bulb being immersed in the liquid:—

	1888.	1888.	1888.	1899.	1899.
Specific gravity,	.8696	.8720	.8754	.8662	.8666
Optical rotation for 100 mm.,	...	...	...	+12.75°	+14.0°
Refractive-index,	...	...	...	1.4685	1.4685
FRACTIONAL DISTILLATION:—					
Barom. pressure in mm.,	...	...	...	758	
First drop collected at ° C.,	157	157.5	157	155	155
5 per cent. at	...	...	...	157	...
10 " "	158	158.5	159	157.5	...
20 " "	158.5	159	160	158	...
30 " "	159	159	161	158.5	...
40 " "	159	160	161	158.5	...
50 " "	159	161	162	158.5	156
60 " "	159	161	162.5	159	...
70 " "	160	161.5	164	160	...
80 " "	161	163	164.5	161	...
90 " "	163	167	176	163.5	...
93 " "	...	...	200	167	160
96.3 " "	...	200	...	172	...
97.3 " "	200	...	...	...	165
97.5 " "	...	...	...	174.5	...
Residue,	1.61% thick; treacly.	2.43% clear; treacly.	4.44% deep brown; very viscous.	0.40% yellowish.	... yellowish.
Bromine temperature-reaction,	...	...	...	16.9°	16.5°
Iodine number,	...	...	...	385.8	...
Oil surviving polymerisation, *per cent.*	...	...	...	1.75	3.50

The following figures show the behaviour of two samples of *rosin-spirit* of English manufacture, when 100 cc. measure was distilled in the author's laboratory in 1886, without dephlegmating arrangement, the thermometer being immersed in the liquid:—

	SAMPLE A (Liverpool).	SAMPLE B (Hull).
Specific gravity at 15.5°,	.8703	.8955
Specific rotation, $[\alpha]_D$,	+0.87°	+12.75°
FRACTIONAL DISTILLATION:—		
First drop over at ° C.,	149	150
	PER CENT.	PER CENT.
Distillate below 155°,	4.5	2.0
" " 160°,	9.5	4.5
" " 170°,	19.0	11.0
" " 180°,	33.5	18.5
" " 190°,	57.5	30.5
" " 200°,	69.5	41.5
" " 210°,	74.5	50.0
" " 220°,	77.5	57.5
" " 230°,	81.5	62.0
" " 240°,	84.0	65.5

These figures illustrate the very variable character of commercial rosin-spirit. Sample B had an optical activity equal to most American oils of turpentine, but the results of the fractional distillation show that only a small proportion of true turpentine can have been present.

The following figures, communicated to the author by L. Archbutt, also show the behaviour of samples of turpentine oil, believed to be genuine, when distilled under the conditions already described. A Fahrenheit thermometer was employed, and the Centigrade temperatures shown in the table are calculated from the observed figures:—

	American Oil.			Russian Oil.		
Measure of Distillate from 100 cc.	Range of Temperature, ° C.	Average Temperature ° C.	Number of Samples.	Range of Temperature, ° C.	Average Temperature ° C.	Number of Samples.
1 cc., ...	156.0 to 163.9	160.1	94	161.1 to 164.5	163.1	4
5 cc., ...	156.5 to 165.0	161.0	103	163.9 to 169.4	167.0	8
90 cc., ...	162.0 to 176.4	169.7	103	177.2 to 188.9	181.6	8
95 cc., ...	162.8 to 186.0	174.1	103	181.7 to 215.5	190.8	8
96½ to 98 cc., ...	163.9 to 205.5	180.4	103	187.8 to 208.9	199.5	7

The figures given in the table on page 489 were also obtained by L. Archbutt by the examination of various turpentine adulterants and substitutes.

According to J. McCandless (*Jour. Amer. Chem. Soc.*, xxvi, 981; abst. *Analyst*, 1904, p. 333), adulteration with refined wood-spirits (wood turpentine) may be detected as follows, after kerosene has been shown to be absent by the polymerisation process (page 490):—100 cc. of the oil is slowly distilled with a low flame, and the refraction figure of the first 0.5 cc. measured at 25° C. In the case of genuine turpentine oil this is never below 60°, usually 61° to 63°. Several samples of wood turpentine showed readings from 57° to 59°. Wood turpentines which do *not* show a low initial reading nearly always show a high reading on the final portion of the distillate. For the 97th and 98th cc. of the distillate the reading in the case of a genuine sample never exceeds 77, according to McCandless, and is usually much less, whilst with wood turpentine the reading may reach 90. A further distinction noticeable during distillation is that while about 95 per cent. of oil of turpentine generally distils below 165° C., this proportion of distillate is not reached in the case of wood turpentines until a much higher temperature is attained.

For the approximate determination of petroleum naphtha in oil of turpentine and its isolation therefrom, H. E. Armstrong

CHARACTERS OF ADULTERANTS AND SUBSTITUTES OF TURPENTINE OIL.

	Rosin Spirit. A.	Rosin Spirit. B. Old Sample.	Rosin Spirit. Rectified.	Camphor Oil.	Eucalyptus Oil.	So-called "Canadian Turpentine." A.	So-called "Canadian Turpentine." B.	"Terebo."	"Imported Spirit."	"Blended Turpentine."	"English Distilled Turpentine."
Specific gravity at 15.5° C.,	0.8569	0.8884	0.8838	0.9135	0.8902	0.8185	0.7844	0.8263	0.8057	0.7982	0.8188
Distillation temperature; ° C.:											
1 cc.,	148.9	142.2	160.6	180.0	129	172.2	117	152.2	154.0	151.5	155.6
5 cc.,	155.0	150.0	167.8	188.3	162	173.9	119	156.7	156.0	153.0	156.7
90 cc.,	197.2	249.0	279.4	226.1	189	272.2	160	263.3	224.4	189.5	196.7
95 cc.,	210.0	..	310.0	234.4	201	300	162	315.6	235.6	202.0	205.0
Iodine number, per cent.,	272.6	178.5	166.9	136.2	116.0	172.8	162.8	58.2	2.6	31.8	107.4
Oil surviving polymerisation tests (page 490);											
Per cent.,	4.4	..	..	..	..	46	54.9	..	..	..	..
Specific gravity,	..	..	..	..	..	0.766	0.725	..	..	..	..
Flash-point (Abel test), ° F.,	..	..	86	..	..	..	37	72	78	79	81

	"English Turpentine."	"Siberian Turpentine."	"South American Turpentine."		Turpentine Substitute.	Turpentine Substitute.	"Beadless Solvent."	"Beadless Solvent." *	Petroleum Distillate.	"Turpolene."	"Patent Turpentine," 6 Samples.
Specific gravity at 15.5° C.,	0.8570	0.8603	0.8227	0.8164	0.8162	0.8238	0.8072	0.8093	0.7992	0.8189	0.8005 to 0.8220
Distillation temperature; ° C.:											
1 cc.,	151.0	162.8	157.8	154.5	164.4	102.8	156.7	162.8	157.8	160.0	154.4 to 163.3
5 cc.,	153.9	164.4	158.9	155.0	167.2	165.0	159.4	163.9	158.9	163.3	160.0 to 170.6
90 cc.,	181.1	176.7	193.9	188.3	222.8	218.9	226.7	225.6	192.8	222.2	232.0 to 250.0
95 cc.,	187.8	181.1	206.7	203.3	231.1	227.2	238.9	236.1	201.1	229.4	246.1 to 261.1
Iodine number, per cent.,	273.7	266.8	121.0	116.0	20.3	55.2	4.8	4.9	4.0	39.4	12.0 to 21.6
Oil surviving polymerisation tests (page 490);											
Per cent.,	..	4	..	..	..	..	..	..	..	..	..
Specific gravity,	..	..	..	..	..	..	..	..	..	..	..
Flash-point (Abel test), ° F.,	78	101	87	83	86	90	85	91	91	85	72 to 84

(*Jour. Soc. Chem. Ind.*, i, 480) recommends a process dependent on the ready and nearly complete polymerisation of oil of turpentine by sulphuric acid, and the comparative indifference to such treatment of the paraffins which form the greater part of petroleum spirit. The method as modified by L. Archbutt is as follows: 500 cc. of the sample of turpentine oil is placed in a stoppered bottle and treated with 120 to 170 cc. of a mixture of two measures of strong sulphuric acid with one measure of water (2:1). The mixture is cautiously agitated at first, the bottle being kept thoroughly cool by a current of cold water. The turpentine is gradually converted into a viscid oil, and when this has taken place, and no more heat is developed on repeated agitation, the liquid is transferred to a separator and the acid layer tapped off. The oily layer is then transferred to a flask and subjected to steam-distillation. When all that is volatile in a current of steam has passed over, the oily portion of the distillate is separated from the aqueous layer and treated with half its volume of sulphuric acid previously diluted with one-fourth of its measure of water (4 : 1). The mixture is agitated as before, the acid liquid separated, and the oily layer again distilled with steam. When genuine turpentine oil has been operated upon, the volatile product of this second treatment consists merely of cymene and a small quantity of a *paraffinoid hydrocarbon* ($C_{10}H_{20}$). It never exceeds 4 or 5 per cent. of the measure of the original sample, and with care is as low as 3 per cent. If the volume notably exceeds 5 per cent. it is advisable, as a precaution, to repeat the treatment with 4 : 1 acid. In any case, the residual oil should then be violently agitated with four times its volume of undiluted sulphuric acid at 60° C., this treatment being preferably repeated. The residual hydrocarbon is then separated, steam-distilled, and again measured, when the surviving oil from pure turpentine oil, either American or Russian, will not exceed 1.5 per cent. by measure of the original sample. Any excess over this proportion represents the *minimum* admixture of *petroleum naphtha* present.[1]

Shale naphtha suffers considerably by the foregoing treatment with acid, and cannot be satisfactorily determined by the process. Its proportion is best deduced from the results of a bromine titration; but the determination is at best only approximate.

Evidence of the presence of *rosin-spirit* is also afforded by the increased yield of hydrocarbons on treatment with 4 : 1 and concentrated sulphuric acid, as rosin-spirit also yields a cymene and paraffinoid hydrocarbon on treatment with 4 : 1 acid. But

[1] H. Herzfeld employs a somewhat similar method, using strong and fuming sulphuric acid for the polymerisation of the turpentine oil (see p. 491), when the mineral adulterants separate on standing.

no sharp determination can be effected by the method, which would even allow a considerable proportion of the admixture to escape detection. The cymene from rosin spirit being isomeric with that from turpentine, proof of the presence of rosin spirit might possibly be obtained by examining the cymene produced.

The following modification of Armstrong's method has been suggested by J. M. McCandless (*Jour. Amer. Chem. Soc.*, xxvi, 981; and private communication) as a means of detecting small quantities (1 per cent. and over) of petroleum products. The method depends upon the observation of the refractive-index (in the Zeiss butyro-refractometer) of the unpolymerisable residue: 100 cc. of the oil is placed in a 600 cc. flask, and gradually mixed with 50 cc. of concentrated sulphuric acid with constant cooling and agitation. Twenty-five cc. of water is then added, and the contents of the flask distilled in a current of steam until a total distillate of 100 cc. is obtained. The refractive index is now determined on a few drops of the separated oil in the distillate. The remainder is measured approximately, and violently agitated with an equal volume of fuming sulphuric acid in a dry stoppered flask. The resulting mixture is poured into cold water, the oil separated, and steam-distilled until 100 cc. of distillate has been obtained. The refractive-index of the distilled oil is again taken, after which the remainder is treated with twice its volume of fuming sulphuric acid, and the foregoing operations repéated. Expressed in terms of the centesimal scale of the refractometer (at 25° C. with sodium light), the oil from the third polymerisation never gives a lower reading than 30 in the case of pure oil of turpentine or wood spirits, while with oils containing only 1 per cent. of kerosene the reading is as low as 25, and can be slowly reduced to 22 by continued treatment with fuming sulphuric acid. The method is not strictly quantitative, but the final volume obtained may be regarded as the minimum proportion of petroleum present, if the refractometer reading does not exceed 22. Adulteration with petroleum naphtha or kerosene of low flash-point results in still lower readings.

W. M. Burton (*Amer. Chem. Jour.*, xii, 102) recommends that, instead of polymerising the oil by sulphuric acid, the sample should be treated with cold concentrated nitric acid, whereby the turpentine is readily oxidised to various acids of the aliphatic and aromatic series soluble in hot water, while petroleum is but slightly affected. Burton recommends for the operation the use of a flask of 750 cc. capacity, fitted with a doubly perforated cork. Through one hole is inserted the tube of a tapped funnel having a capacity of 100 cc., while the other carries a tube connected with an inverted condenser. About 300 cc. measure of nitric acid of 1.5 specific gravity is placed in the flask, and 100 cc. of the sample of oil of turpentine measured into the separa-

ting-funnel. The flask is immersed in cold water and the turpentine then allowed to fall drop by drop into the acid, with frequent agitation. Violent action takes place with evolution of red fumes. When the turpentine oil has all passed into the flask the apparatus is allowed to stand until all action is over. The contents are transferred to a large separating-funnel and treated with successive portions of *hot* water. In this way all the products resulting from the action of the acid on the terpenes are removed, whilst any petroleum paraffins remain insoluble in water and can be readily separated and measured. Benzene if originally present is converted into nitrobenzene in this process and can be steam-distilled from the aqueous liquid, and then rectified by redistillation.

J. H. Long states that Burton's method has given him fairly good results. In the author's laboratory, even when very carefully conducted, the process has been found far too *dangerous* for general use, actual explosions having occasionally occurred. This is especially liable to happen when pure or nearly pure turpentine is under treatment. With largely adulterated samples, the petroleum acts as a diluent, and the action is comparatively moderate. As a supplementary treatment, after applying the Armstrong process, the author finds the Burton method to be occasionally useful. It should never be applied direct.

A good indication of the presence and amount of certain adulterants of turpentine oil is obtainable by distilling the sample in a current of open steam. Unless it has been freely exposed to the air for some time, genuine turpentine oil leaves a mere trace of non-volatile matter, but old samples may leave a small proportion (up to about 3 per cent.) of resinous matter, which solidifies on cooling. According to Armstrong, if more than 0.4 per cent. of non-volatile residue is left after steam distillation, it consists, as a rule, of *petroleum oil*. This is recognisable by its comparatively low density (0.800 to 0.850, colophene being 0.940) and more or less marked blue fluorescence when dissolved in ether. The residue from genuine old turpentine oil is readily oxidised and dissolved by dilute nitric acid, while the petroleum product is more or less nitrated without altering much in volume. *Rosin oil* would be recognisable by the Storch-Morawski reaction (page 177).

The oil which distils over in a current of steam will consist of the genuine oil of turpentine, together with the more volatile portions of any adulterants, and the presence of any shale or petroleum naphtha will be indicated by the low specific gravity of the oily portion of the distillate, after separation from the water which condenses with it.

The use of rosin-spirit as an adulterant of turpentine oil is

frequent, and if used in small proportion is difficult of detection. The odour suffices to indicate the presence of an inferior spirit, but is useless if the refined article has been employed. The behaviour on distillation varies, but the temperature rises regularly throughout the process, and no considerable fraction is obtained at a constant temperature of 158° to 160° C., as in the case of American turpentine oil. Very often there is a notable residue of viscid oil left on steam-distillation. The bromine-absorption of rosin-spirit is somewhat lower than that of turpentine oil, but the difference is not sufficiently marked or constant to serve as a distinction. The optical rotation of commercial oil of turpentine is too variable to allow of the optical activity being employed for the determination of the proportion of rosin spirit present.[1] The reduced flash-point is a trustworthy test for the presence of rosin spirit.

F. Evers (*Chem. Centr.*, 1898, i, 865) states that the Custom House official method for the examination of oil of turpentine, depending upon the increase of temperature with an equal volume of fuming hydrochloric acid (sp. gr., 1.19), is useless owing to the facts that the older and more resinified the oil, the greater the rise of temperature with hydrochloric acid; and that mixtures of such oils with "patent" oil of turpentine gave results similar to those of genuine samples. Evers employs a method for the detection of such substitutes for oil of turpentine, depending on the fact that the substitutes do not combine with bromine, while oil of turpentine takes up an appreciable quantity. His method has been improved by Schreiber and Zetzsche (*Chem. Zeit.*, 1899, page 686), who recommend the following procedure:— The sample is first dissolved in sufficient alcohol of about 95 per cent. strength to yield a 2 per cent. solution. Two other solutions are required,—one containing 50 grammes of potassium bromide and 15 grammes of potassium bromate in 1 litre of water; and a dilute sulphuric acid solution, 1:3. Twenty cc. of the turpentine solution in alcohol is treated with 20 cc. of each of these solutions, and the mixture shaken for half a minute, the temperature being kept near 20°. Genuine oil of turpentine decolorises this solution.

[1] According to H. E. Armstrong, the products of the distillation of rosin are always optically inactive; but this is certainly not uniformly the case with the ordinary commercial products. The specific rotation of rosin-spirit in the author's experience ranges from 0° to +13°. The heavier fractions obtained by the distillation of rosin, commonly known as "rosin oil," are viscous liquids of high boiling-points, and quite unsuited for the adulteration of turpentine oil. Hence the recommendation of A. Aignan (*Compt. rend.*, cxxiv, 1367) for the determination of "rosin oil" in oil of turpentine has little practical interest. Similarly, the index of refraction, the observation of which is recommended by M. Zune (*Compt. rend.*, cxiv, 490) for the determination of "rosin oil," has little value in practice.

A. McGill (*Canadian Inland Revenue Bulletin No.* 79, p. 34) finds the improved method fairly satisfactory. Coal oil, gasoline and rosin oil failed to decolorise the bromine solution; 20 per cent. of coal oil could easily be detected in admixture with genuine turpentine oil, but 10 per cent. gave only a doubtful indication.

A test for rosin-spirit in turpentine oil has been described by P. H. Conradson (*J. S. C. I.*, 1897, p. 519). An aqueous solution of sulphurous acid, when shaken with rosin spirit, imparts to the latter a beautiful yellow colour, the aqueous layer remaining colourless. Pure oil of turpentine, benzene, gasolene, and "160° oil," give no such coloration. After standing for several hours, the yellow colour obtained with rosin-spirit changes on the surface to brown and further to blue, finally assuming a reddish or bluish-brown colour. Oil of turpentine shows no change of colour on standing with sulphurous acid solution. A snow-white emulsion is produced on shaking the mixture and the emulsion breaks up very slowly. A sample of "wood turpentine" examined by Conradson gave the above coloration with sulphurous acid, had a specific gravity of 0.845, a flash-point below 80° F., and was evidently adulterated.

The *iodine absorption* of turpentine oil is capable of furnishing valuable information and may aid in distinguishing between American and Russian oil of turpentine. L. Archbutt, as the result of a large experience, recommends the employment of the Wijs method. Hübl solution, unless recently prepared and of full strength, does not give the maximum absorption. The time allowed for the reaction between the Wijs solution and the oil of turpentine must be exactly the same for all samples, as this factor has a great influence upon the amount of iodine absorbed. Although absorption of iodine is very rapid at first, the maximum absorption ($C_{10}H_{16}+2I_2=372$ per cent. iodine) is not reached for many hours.[1]

[1] *This is shown by the following results communicated to the author* by Archbutt. In each experiment 0.1 gramme of oil of turpentine was used, and 30 c.c. of the Wijs' solution, containing 0.7674 gramme of iodine.

Time of Action.	Wijs' Value of American Oil of Turpentine.		
	A.	B.	C.
5 minutes	277.4		
10 minutes	290.3		
20 minutes	316.1	324.2	318.7
1 hour	338.1		
6 hours	359.8		
18 hours	379.4	379.3	373.4
24 hours	382.6		

L. Archbutt recommends 20 minutes' action as the most convenient, and states that samples of American oil of turpentine which absorb less than 320 per cent. of iodine from Wijs' solution in this time should be regarded with suspicion. For the determination, a few milligrammes more than 0.5 gramme of the sample is weighed into a 50 cc. flask, which is then filled to the mark with chloroform. The solution having been well mixed, 10 cc. is transferred to a stoppered bottle and mixed with 30 cc. of Wijs' solution containing not less than 0.7 gramme of *iodine.*[1] *After exactly 20 minutes' action an excess of potassium* iodide solution is added and the liquid is titrated in the usual manner.

The iodine values of various substitutes and adulterants of oil of turpentine are given on page 489. These were determined by the Hübl method.

The *bromine thermal test* (O. Hehner, *J. S. C. I.*, 1897, p. 87) also affords a rapid method of obtaining an approximation to the iodine value, but presents no advantage over Wijs' modification of the latter.

The value of pure oil of turpentine (American) has risen considerably of late years, and it appears probable that a serious scarcity of the article will before long prevail. Some districts (notably North Carolina) in which the distillation of the oil formed an extensive industry a few years ago, have now almost ceased to produce it. As a consequence of these conditions, refined Russian turpentine oil is now being employed with good results for many purposes. In addition, during the last three or four years a product termed "wood turpentine" ("pine turpentine" or "stump spirits") has been manufactured by distilling pine-wood scraps with superheated steam at 260° C. Two qualities of oil are obtained, and both grades of mechan-

The following results have also been communicated by Archbutt:—

Time of Action.	Iodine Absorption (Wijs).						
	American Turpentine Oil.				Russian Turpentine Oil.		
	Number of Samples.	Highest.	Lowest.	Average.	Number of Samples.	Highest.	Lowest.
20 mins., . . .	30	348.1	309.3	329.0	2	295.5	276.5
18 hours, . . .	18	395.2	364.0	377.2	2	354.7	333.5

[1] At the end of the experiment, the unabsorbed iodine should be at least equal in amount to that absorbed, and not more than 5 per cent. in excess of the amount absorbed (Archbutt). If these conditions do not obtain, the test is repeated with suitably altered proportions of iodine and turpentine oil.

ically refined oil are stated by the manufacturers to be equal to true oil of turpentine in most respects, though this is doubtful. There is no doubt that considerable quantities of this product are being sold in England as pure turpentine oil.

Wood-turpentine oil is stated to have a similar specific gravity, boiling-point and distillation characters as pure oil of turpentine. J. M. McCandless has pointed out certain small differences in these properties (see page 488). There is, however, a marked difference in odour between the two products. Wood turpentine oil is said to contain both terpenes and alcoholic constituents. According to R. A. Worstall (*J. S. C. I.*, 1904, page 302) wood turpentine may be readily detected by its low iodine-number, as determined by the Hübl solution after 12 hours action in the dark with a large excess of iodine. Under these conditions, Worstall found the average absorption of pure turpentine oil to be 375 per cent. of iodine, while wood turpentine gave the value 212, and a sample of turpentine oil containing even 5 per cent. of wood turpentine yielded the low figure of 360 per cent. of iodine absorbed. The figure 370 is suggested by Worstall as the minimum limit of iodine absorption for genuine turpentine oils under the above conditions. The results of J. M. McCandless (*loc. cit.*) show that the iodine absorption of wood turpentine may thus vary from 282 to 352 per cent.

The following description of the characters of genuine oil of turpentine is substantially that of T. Macfarlane (*Bulletin No. 79, Laboratory of the Inland Revenue Department, Canada*), and is based upon the results of a large number of analyses:— Oil of turpentine is a clear and practically colourless liquid, but is made decidedly opaque by shaking with 0.1 per cent. of water, and perfectly clear samples give, when distilled, a first fraction of 10 per cent., which is opaque but which settles clear in a few hours. The odour of turpentine oil is peculiar and characteristic, quite distinct from that of gasoline, rosin spirit or acetone, and capable of disguising these odours to the extent of 10 per cent. admixture. The specific gravity of turpentine oil lies between 0.860 and 0.880 (usually about 0.870) at a temperature of 15.5° C., but samples which have been long exposed to air may have a higher gravity. When distilled, the first fraction amounting to one-tenth of the original volume has a gravity between 0.856 and 0.870. The gravity of the residual tenth (undistilled) should not exceed 0.900. The boiling-point should lie between 154° and 158° C., and 90 per cent. should distil below 180° C. On evaporating the sample at 100° C., the fixed residue should not exceed 2 per cent. The flash-point by Abel's test should be about 32° C. Turpentine oil should dissolve completely in an equal volume of glacial acetic acid, and the first 10 per cent. fraction obtained by distillation should similarly dissolve. One cc. of a solution of 1 part of as-

phaltum in 10 of turpentine oil should not, after filtration, be rendered translucent when diluted with 9 cc. of turpentine oil. The refractive-index at 20° C. should lie between 1.4667 and 1.4722; while that of the first fraction (of 10 per cent.) should not exceed 1.4700. Concentrated sulphuric acid should polymerise and char the oil at 100° C. Oil of turpentine should respond to the bromine test of Schreiber and Zetzsche (described on page 493).

The German law requires that oil of turpentine employed for the denaturation of alcohol shall have the following characters: Specific gravity, between 0.855 and 0.865 at 15° C. When 100 cc. measure is fractionally distilled in a metal flask furnished with a dephlegmator, not more than 5 cc. must come over below 150°, but at least 90 cc. at 160°. When 20 cc. measure of the sample is shaken vigorously with an equal measure of water, and the liquid allowed to stand till clear, the upper (turpentine) stratum must measure at least 19 cc.

A. and P. Andouard (*J. Pharm. Chim.*, xv, 99) have described a petroleum product from America, known as "white spirit," which is much used in France for the adulteration of oil of turpentine. "White spirit" has a violet-blue fluorescence, and a specific gravity of 0.807. It is almost optically inactive, and begins to distil between 150° and 160°, the last fractions having a high boiling-point. It leaves about 40 per cent. of residue at 205° C.

An article sold in commerce as "*German oil of turpentine*" is stated to consist of a mixture of camphor oil with petroleum fractions.

Banner's "*turpentine substitute,*" according to the specification (*Brit. Patent*, 1885, No. 12,249), is essentially prepared by selecting, during the distillation of petroleum, coal oil, or other similar heavy hydrocarbons, groups of fractions containing hydrocarbons of a specific gravity ranging from 0.730 to 0.840. The characters of six samples examined by L. Archbutt are given in the table on page 489, under the heading "Patent Turpentine."

TEREBENE, according to the British and United States Pharmacopœias, is a mixture of dipentene and other hydrocarbons, obtained by agitating oil of turpentine with successive quantities of sulphuric acid until it no longer possesses optical activity. The product is then distilled with steam. Some manufacturers of terebene do not carry the process sufficiently far to produce a totally optically-inactive product.

Terebene is a colourless liquid with an agreeable thyme-like odour and an aromatic terebinthinate taste. It is only slightly soluble in water, but dissolves in three volumes of 90 per cent. alcohol. On exposure to air and light, terebene gradually resinifies, becoming yellowish and acid. The specific gravity of tere-

bene ranges from 0.862 to 0.866 at 15.5° C. Terebene should be optically inactive. The British Pharmacopœia requires that terebene should not contain more than 15 per cent. of constituents distilling below 165°, and that all except a slight viscid residue should distil between 156° and 180° C. (absence of excess of resin). According to the U.S. Pharmacopœia (8th Rev.), terebene distils between 155° and 165° C. Terebene should not redden moist blue litmus-paper, and should yield only a very slight non-volatile resinous residue on evaporating 10 cc. in an open dish at 100° C.

Tyrer and Wertheimer (*Pharm. Journ.*, 1900, ii, 101) find that, with due precautions, American oil of turpentine yields terebene answering the official requirements, except in the respects that 5 per cent. remains undistilled at 180°, and that no fraction is absolutely devoid of optical activity. Two samples of "terebene" examined by these observers boiled considerably above the official limits, and had thus been distilled by steam under pressure or by a direct flame. Terebene from French oil of turpentine was found on fractional distillation to yield 28 per cent. of a mixture of optically-inactive substances.

Painters' terebine, which is a dark brown solution of manganese and lead soaps in oil of turpentine, used as a drier by painters, must not be confounded with *terebene.*

Wormseed Oil. Oil of Levant Wormseed.

This oil should not be confused with the oil of "American wormseed," which is in reality chenopodium oil.[1] Oil of Levant wormseed is distilled from the unexpanded flower-buds of *Artemisia maritima.* According to E. J. Parry, other species probably contribute to the commercial oil.

The true wormseed oil is a thick yellow or brownish oil, having the camphoraceous odour of cineol. It has a specific gravity of 0.930 to 0.935.[2] It is slightly lævo-rotatory. When rectified, the oil is colorless.

The constituents of this oil, so far as known, are cineol, together with another oxygenated body which has not yet been identified, and, possibly, dipentene.

[1] Chenopodium Oil is the product of the distillation of the fruit from *Chenopodium ambrosioides* (*C. anthelminticum* Linn.). It is a light yellow oil of specific gravity 0.900 to 0.975 (according to the U. S. Pharmacopœia, 0.965 to 0.985 at 25° C.), and has an optical rotation of —5° to —18° for 100 mm. Very little is known of its composition, but in all probability it contains limonene. The oil is official in the U. S. Pharmacopœia (8th Rev.), which requires it to be soluble in 5 volumes of 70 per cent. alcohol, and to have an optical rotation not exceeding —5° for 100 mm. at 25° C.

[2] These figures represent the usual limits of specific gravity of the oil. The outside limits, as given by Gildemeister and Hoffmann (*The Volatile Oils*) are 0.915 to 0.940.

Wormwood Oil. OIL OF ABSINTHE.

This oil is obtained by the distillation of the green herb *Artemisia absinthium*, which is extensively cultivated in North America. The oil is used in medicine both internally and externally, and it is a constituent of the liqueur *absinthe*. It is frequently designated oil of absinthe.

Oil of wormwood is of a dark green or greenish-blue colour, and has a strong characteristic odour and acrid taste. Its specific gravity varies from 0.925 to 0.955.[1] Adulteration of this oil with oil of turpentine may therefore be inferred from its lowered specific gravity. Since oil of wormwood contains only slight traces of pinene, the presence of turpentine in the oil may also be detected by the characters of the first 10 per cent. of the distillate, as recommended by Schimmel & Co. The distillate from pure wormwood oil dissolves in 2 volumes of 80 per cent. alcohol to a clear solution. Very small additions of oil of turpentine, which is a frequent adulterant of wormwood oil, may thus be detected.

The principal constituent of the oil is the ketone thujone (see page 380). Thujyl alcohol is also present to a considerable extent, both in the free state and in combination with acetic, isovaleric, and palmitic acids. Phellandrene is present to a very small extent, and pinene only in slight traces. A sample of the pure oil examined by Schimmel & Co. was found (upon acetylation and saponification) to contain 24.2 per cent. of thujyl alcohol, of which 13.9 per cent. was present in the form of esters (equivalent to 17.6 per cent. of thujyl acetate).

JAPANESE WORMWOOD OIL (Yomugi oil), from *Artemisia vulgaris*, is of a bright green colour having a marked odour of cineol. It contains this constituent and probably also thujone. Schimmel & Co. found it to have the following characters: Specific gravity, 0.9101; optical rotation, —13.25°; acid value, 1.56; ester value, 29.81. The oil was not completely soluble in alcohol.

Terpeneless Essential Oils.[2]

By subjecting the essential oils to careful distillation under reduced pressure, there are obtained two main fractions—the

[1] The optical rotation of the oil cannot well be taken owing to its deep colour, but since the chief constituent, thujone, is strongly dextrorotatory, the oil will no doubt be optically active in this direction.

[2] The chief constituents of essential oils, prepared in a pure state (*e. g.*, citral, eugenol, safrol, &c.) have occasionally been termed *terpeneless oils*, but this is manifestly a misnomer. In many cases these products are

hydrocarbons or terpenes of the oils, and the odorous oxygenated portion, which can be kept behind in the distillation apparatus. The terpene fraction has comparatively little or no odour in most cases; while, as a rule, the oxygenated or high-boiling fraction retains all the good qualities of the original oil in a heightened degree. In other words, the oil has been concentrated, and the residual valuable fraction is found to have a far greater solubility coefficient (in alcohol) than the original oil, a fact which is of considerable commercial importance.[1]

Völckel and Schweitzer in 1840, and Haensel in 1876, first pointed out the value of this procedure. Many other observers followed up their researches and the increased usefulness of the terpeneless products has been widely recognised. The terpenes as a class readily oxidise and resinify on exposure to air, and at the same time develop an unpleasant odour and taste. Essential oils, which are thus liable to lose their delicate odour and flavour on keeping, may therefore frequently be stored in a terpeneless state for a long time without deterioration. Thus the terpeneless oils are specially valuable in the manufacture of perfumes, liqueurs and essences, and for medicinal purposes.

The following table shows the physical characters of many of the best-known terpeneless oils. The data are chiefly due to E. J. Parry, though some are taken from H. Haensel's *Reports* (H.). With the exception of the first sample of bergamot oil (see footnote, page 501), all the samples were genuine terpeneless products.

TERPENELESS OIL.	SPECIFIC GRAVITY AT 15.5° C.	OPTICAL ROTATION ° IN 100 MM. TUBE.	VOLUMES OF ALCOHOL REQUIRED FOR COMPLETE SOLUTION.
Angelica root,..	0.951 0.956 (H.).	—3.7 ...	... ...
Angelica seed,..	0.961 (H.).	—1.5	1.8 of 80%. 41 of 70% (H.).
Bay...........	1.034; 1.028 (H.).	...	5 of 60% (H.).

inferior to the real terpeneless oils, though sometimes they are superior to the latter. The two classes should, however, be carefully differentiated and the term "terpeneless oil" restricted to the product properly coming under that description.

[1] In certain cases, distillation at however low a pressure would cause decomposition of the valuable oxygenated constituents of the oil. Where this is the case, the terpeneless oil is of very little value since it does not represent the unaltered concentrated oil. Some few oils contain so little terpene that the terpeneless oil possesses little advantage over the natural product.

TERPENELESS OIL.	SPECIFIC GRAVITY AT 15.5° C.	OPTICAL ROTATION ° IN 100 MM. TUBE.	VOLUMES OF ALCOHOL REQUIRED FOR COMPLETE SOLUTION.
Bergamot [1] (1),..	0.903	—11.25	. . .
Bergamot (2),..	0.8875	—9.25	8 of 60% (H.).
Bergamot (3),..	0.885	—7.9	. . .
Caraway,[2]	0.962 to 0.965	+55 to +59	(B. pt., 223°–225°.)
Citronella,.....	0.932; 0.912	—5	. . .
Cloves,........	1.072	0	. . .
Eucalyptus,....	0.938 (H.).	—1.7	($[n]_D$, 1.4679).
Fennel,........	0.982	. . .	. . .
Geranium,.....	0.896	—1.9	. . .
Ginger,........	0.909; 0.919 (H.).	. . .	1 of 80%; 45 of 70% (H.).
Juniper,[3].......	0.916	—28.75	. . .
Lavender,......	0.893 to 0.897	—3 to —5	20 of 60% (H.). Contains 18–25% linalol; 30–40% linalyl acetate.
Lemon,[4].......	0.896 to 0.900	—7 to —9	5–20 of 70%; 260 of 60%; contains 42–67% of aldehydes.
Lemongrass,...	0.897	—1.2	. . .
Limes (expressed),..	0.896	—8.6	. . .
Limes (distilled),...	0.920	—2.2	. .
Orange,........	0.894	+5 to +10	2 of 70% (H.).
Peppermint (various),....	. . .	—13 to —28 (H.).	. . .
Pimento,......	1.062	—0.5	. . .
Rosemary,.....	*0.939; 0.944* (H.).	+*10.9* (H.).	. . .
Sassafras,......	1.088	+2	. . .
Spearmint,.....	0.945 (H.).	. . .	70 of 70% (H.)
Wormwood,....	0.922	. . .	2.5 of 70% (H.).

[1] Probably contained artificial linalyl acetate (Parry).

[2] Reasoning from the figures yielded by this oil, Parry concludes that the physical characters usually ascribed to carvone are incorrect; probably the density of carvone is about 0.964 and its optical rotation not more than +60°.

[3] Although free from terpene, this oil of course contains much sesquiterpene.

[4] Burgess and Child have recorded a number of figures showing the composition and behaviour on fractionation of terpeneless oils of lemon (*J. S. C. I.*, 1901, p. 1176).

The "concentrated oil of lemon" on the market contains about 10 per cent. of terpenes and is therefore to be distinguished from the terpeneless oil. True terpeneless oil of lemon is freed from the greater portion of the natural stearoptene by allowing the latter to separate after the distillation of the terpenes; or the oil is prepared by distilling 90 per cent. of natural oil of lemons under reduced pressure, and steam-distilling the residue, when the terpeneless oil comes over practically free from citraptene. *The yield of terpeneless oil is from 5 to 6 per cent.*, containing approximately half its weight of *citral*. (See page 432.)

TABLE

OF CHARACTERS AND CONSTITUENTS OF ALL THE BETTER-KNOWN ESSENTIAL OILS.

*The following tabular list of the characters of the better-*known essential oils has been compiled from data given in E. J. Parry's *Chemistry of Essential Oils, etc.;* Bush & Co.'s *Reports (B. & Co.);* Schimmel & Co.'s *Semi-Annual Reports (S. & Co.);* and from current literature.

The table was prepared, at the request of the Author, by A. R. Tankard and John Evans.

TABLE OF ESSENTIAL OILS.

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Acacia.	Flowers of *Acacia cavenia.*	....	....	....	....	Eugenol (40 to 50 per cent.); methyl-eugenol; methyl-salicylate (8 per cent.); benzyl alcohol (20 per cent.); benzaldehyde; geraniol; anisic aldehyde; and probably also linalol, decyl aldehyde, and ionone.	Perfumery.
	Flowers of *Acacia farnesiana.*	....	....	....	....	Similar to above, but eugenol is absent.	
Achillea (see also *Iva Oil*).	Flowering herb of *Achillea coronopifolia.*		0.924	....	A deep blue oil, with an odour of tansy.	....	....
	Herb of *A. nobilis.*	0.26	0.970	....	Camphoraceous odour and bitter taste.		
			0.935	—10.4	Distils at 170°–265°.	Terpenes; a sesquiterpene; *linalol*; *linalyl acetate.*	
Ajowan.	Fruit of *Carum ajowan.*	3.0 to 4.0	0.9175–0.930	+ 1.0 to + 1.5	....	Thymol, 40–50 per cent.; cymol.	Preparation of thymol.
	S. & Co.	....	0.900–0.930	....	....		
	Herb of *Carum ajowan.*	0.12	0.860	+ 0.7	A light brown oil, sol. in 6 parts 90 per cent. alcohol, with separation of a paraffin.	Thymol (about 1 per cent.); phellandrene (trace).	
Allspice.	(*See Pimento Oil.*)						
Ambrette.	*S. & Co.*	....	0.900–0.905	....	Congeals at 10° C.	....	....
	B. & Co.	....	0.9145	....	Deposits a paraffinoid hydrocarbon.	....	....

Ammoniacum.	The gum-resin from the stem of *Dorema ammoniacum*.	0.3	0.890	slightly +	Distils between 250° and 290° C.	....	....
Angelica.	Root of *Archangelica officinalis*. *B. & Co.*	0.25 to 1.0	0.855–0.905 *0.8925*	+26.7 to +30.1 *+ 15.0*	Turns yellow on exposure to light. *Saponification number*, 37.7. Distils chiefly between 60°–70° C.	Phellandrene; valeric acid; hydroxy-pentadecoic acid.	Preparation of liqueurs.
	Fruit of *A. officinalis*.	....	0.850–0.900	+ 11 to + 12	Pale yellow; darkens in colour with age.	Phellandrene; valeric acid; hydroxy-myristic acid.	....
Japanese.	Root of *Angelica refracta* and *Angelica anomala*.	....	0.915	....	At 10° C., crystals of a fatty acid separate, *melting* at 62–63° C. Oil distils between 170°–300° C.	....	....
Angostura.	Bark of *Galipea cusparia*.	1.5	0.930 to 0.960	—36 to —50	....	Cadinene; galipol, $C_{15}H_{26}O$, 14 per cent.; galipene; an oxygenated body; pinene.	Medicine.
Anise.	Fruit of *Pimpinella anisum*.	1.5 to 6.0	0.980–0.990 (at 17° C.)	to —1.9	*At 15°–19° C. solidifies* to a white, crystalline mass (anethol). B. pt., 234° C.	*Methyl-chavicol*; about 90 per cent. anethol; anise-ketone.	Medicine; flavouring agent.
Anise.	Bark from Madagascar. Botanical origin uncertain.	....	0.969	—0.8	....	Methyl-chavicol; small amount of anethol.	....
Anise, Star (Chinese) [Badiana Oil].	Fruit of *Illicium verum*.	5.0	0.980–0.990 (at 17° C.)	—2 to + 1	At 12–18° C. solidifies.	Anethol; anise aldehyde and ketone; anisic acid; methyl-chavicol; Estragol; pinene; phellandrene; safrol; ethyl-ether of quinol.	Medicine; flavouring agent.
Anise, Star (Japanese) [Badiana Oil].	Leaf of *Illicium religiosum*.	0.44	1.006	—8.1	....	*Anethol*; *safrol*; *eugenol*; a terpene (limonene?).	....

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Apopin (Shu-yu).	From one of the *Lauraceæ*.	....	0.9279	+ 17.3	....	Camphor; eugenol; safrol; cineol; dipentene.	....
Arnica.	Rhizome of *Arnica montana*.	1.0	0.990–1.000	—2.0	Yellow colour, becoming darker with age.	Dimethyl ether of thymoquinol (80 per cent.); Phlorol iso-butyrate, 20 per cent.); a very little phloral methyl-ether.	Medicine.
Artemisia.	Herb of *Artemisia glacialis* (so-called *Genepi des Alpes*).	....	0.969	....	Distils at 195–310° C. Solidifies at 0° to a buttery mass.	Cineol; a fatty acid, M. pt., 61° C.	....
	Herb of *Artemisia vulgaris* (common mugwort).	....	0.907; 0.920	....	....	....	....
Asafœtida.	The gum-resin from root of *Ferula fœtida*, etc.	3.0 to 4.0	....	—9.25	....	Pinene (?); a substance containing $C_{10}H_{16}O$; the sulphuretted bodies; $C_7H_{14}S_2$; $C_8H_{16}S_2$; $C_{10}H_{20}S_2$; $C_{10}H_{18}S_2$; a blue fraction.	....
Asarum Canadense.	Rhizome and root of *Asarum Canadense* ("Canada snake-root").	3.0 to 5.0	0.930–0.960	....	Yellowish - brown oil.	Pinene; asarol 35 per cent., but no asarone; methyl-eugenol, 35 per cent.; asarol acetate and valerate; a deep blue fraction.	Perfumery.
Asarum Europæum.	Rhizome and root of *Asarum Europæum* ("Asarabacca").	1.0	1.046–1.068	....	Thick, brownish liquid.	Pinene; methyl-eugenol; asarone, but no asarol; a blue fraction.	Perfumery.
Backhousia citriodora.	Leaves of *B. citriodora*.	To 4.	0.895	Inactive or slightly —.	R. Index, 1.4890. Distils 215°–230°C.	Aldehydes, 95 per cent. (chiefly citral); sesquiterpenes (traces); an amyl ester (?).	Source of citral.
Badiana.	(See *Anise Oils*.)						

Balsam-fir.	Leaves of *Abies balsamea.*	....	0.894	—29	....	Bornyl acetate; pinene (?).	....
Basil (Basilicum).	Fresh herb of *Ocymum basilicum.*	....	0.909–0.990	—22 to + 10	....	Pinene; cineol; camphor; linalol; methyl-chavicol.	....
Bay (Myrcia).	Leaves of *Pimenta acris.*	2 to 3.0	0.975–0.990	....	Clove-like odour and spicy taste.	Eugenol and chavicol (60–65 per cent.); methyl-chavicol; methyl-eugenol; citral; myrcene; *l*-phellandrene.	....
	S. & Co.	....	0.965–0.985	Up to —2.			
Californian.	Leaves of *Laurus Californica.*	4	0.930 to 0.950	....		Cineol; terpineol (?).	....
Bergamot.	Fresh fruit of *Citrus bergamia* (by expression).	....	0.880–0.885	+ 9 to + 15	Greenish or greenish-yellow liquid. Begins to distil at about 170° C.	Limonene; dipentene; linalol; *linalyl acetate* (36–39 per cent.).	Perfumery; *perfuming* soaps.
Betle.	Leaves of *Piper betle.*	....	....	....	....	Betle-phenol (para-eugenol); cadinene; sometimes chavicol.	....
	Dried leaves from Siam.	....	1.034	....	....	....	....
	Fresh leaves from Manila.	0.5 to 1.0	1.044	....	....	....	....
	Fresh leaves from Java.	....	0.958	+ 2.8	....	....	....
Boldo.	Leaves of *Peumus boldus.*	1.6	0.876	—6.5	....	Eugenol (?); pinene; cuminal; acetic esters; an oxygenated body; a sesquiterpene.	....
	Dried leaves.	2.0	0.915 to 0.945	....	Distils 175°–250°.		
Boronia.	*Boronia polygalifolia.*	....	0.839	+ 10	Sweet odour resembling tarragon and rue. Distils largely between 150° and 190° C.	....	Perfumery.
Buchu.	Leaves of *Barosma serratifolia.*	1.0 to 2.0	0.944	....	Strong, mint-like odour.	Diosphenol (small amount); limonene; dipentene; menthone.	....
	Leaves of *B. betulina.*	....	0.969 0.9573	.... —48	The gravity given refers to that of the oil after the diosphenol had separated at ordinary temperature.	Diosphenol (large amount); otherwise like above oil.	

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Cajuput.	Leaves of *Melaleuca leucadendron.*	....	0.920–0.930	To —2.	When crude, is a bluish-green liquid with a camphoraceous odour and somewhat bitter taste. Green colour usually due to traces of copper.	Cineol, about 50 per cent.; terpineol; terpenyl acetate; pinene (?); valeraldehyde (?); benzaldehyde (?).	Medicine.
	Brit. Pharm.	....	0.922–0.932				
Calamus.	Fresh herb of *Acorus calamus* (Sweet Flag).	0.2	0.964	+ 20.7	Closely resembles the oil from the rhizome.	....	....
	Rhizome.	0.8 to 5.0					
	German, Fresh Drug.	....	0.960–0.970	+ 20 to + 31	Thick brownish liquid with a bitter taste.	Pinene (?); acetic, œnanthilic, heptylic and palmitic acids; eugenol; asaryl aldehyde; asarone; calameone $C_{15}H_{26}O_2$; parasarone; and a bluish fraction.	Medicine; preparation of liqueurs.
	German, Dry Drug.	....	0.960–0.980	+ 15 to + 21			
	Japanese.	....	0.985–1.00	....	Much more soluble in dilute alcohol than the German variety.	....	....
Camphor.	By-product in preparation of common camphor by the distillation of wood of *Cinnamomum Camphora.*	....	0.870–1.040	....	Very variable in character. Fractional distillation affords commercial light camphor oil (sp. gr. 0.920) and heavy oil (0.970).	Pinene; phellandrene; dipentene; cineol; camphor; terpineol; safrol; eugenol; cadinene; camphene (?).	....
	Leaves of camphor tree.	....	0.932	+ 4.9	Liquid portions (separated from camphor) have properties of above camphor oils.	Large amount of camphor.	....

Camphor-Wood (Venezuelan).	From Venezuelan wood of unknown origin.	1.15	1.155	+ 2.7	Solidifies in a crystalline mass (apiol) at ordinary temperatures.	Apiol (parsley-apiol), 90 per cent.	....
Cananga.	(See *Ylang-Ylang Oil.*)						
Canella.	Bark of *Canella alba.*	0.7 to 1	0.922	....	Spicy odour and taste.	Pinene; caryophyllene; cineol; eugenol.	....
Caparrapi.	Wood of *Nectandra caparrapi.*	....	0.914–0.916	Slight.	Pale yellow to brownish-red oil. Acid reaction to litmus. Odour *sweet and resembling* chloral.	Caparrapic acid, $C_{15}H_{26}O_3$ (monobasic), melting at 84.5° C.; a sesquiterpene alcohol (Caparrapiol).	*Copaiba balsam* substitute.
Caraway.	Fruit of *Carum Carvi.*	....	....	....	....	Dextro-limonene; carvone; with *possibly carvacrol.*	Medicine; preparation of liqueurs; flavouring agent.
	S. & Co.	3 to 7	0.905–0.915	+ 75 to + 85	Characteristic odour and spicy taste. Distils mainly above 200°; not more than 15 per cent. should distil below 185°.	....	
	Brit. Pharm.	....	0.910–0.920	....		....	....
Cardamoms.	Seed of *Elettaria repens.*	....	....	....	....	Terpinene; dipentene; limonene; terpineol; acetic esters.	Preparation of liqueurs.
	(Ceylon.) *S. & Co.*	2 to 8	0.895–0.905	+ 12 to + 13	Camphoraceous odour and taste.		
	B. & Co. (Bengal.) *S. & Co.*	....	0.930–0.940 0.920	+ 30 —12.7	Distils chiefly below 220° C.	Large amount of cineol.	....
Carrot (*Wild*).	Fruit of *Daucus carota.*	....	0.870–0.930	—13 to —37	Sharp taste.	Pinene; terpineol (?).	....

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Cascarilla.	Bark of *Croton Eluteria.*	1.0–3.0	0.890–0.930	+ 5	....	Terpenes; palmitic and stearic acids (traces); cascarillic acid (2 per cent.), $C_{11}H_{20}O_2$; traces of eugenol and cresol; and oxygenated bodies.	....
Cassia.	Bark of *Cinnamomum cassia.*	....	1.050–1.065	+ 1 to —1	....	Cinnamic aldehyde, 70–85%; cinnamic esters, &c.	(See p. 44.)
Cedar-leaf (American).	Leaves of Red Cedar, *Juniperus Virginiana.*	....	....	....	....	Limonene; pinene (?); cadinene; borneol; bornyl esters.	....
	Commercial sample.	....	About 0.884	—8.25	Savin-like odour. Colourless.	....	....
	S. & Co.		0.886	+ 59.1	Pale greenish-yellow. Medicinal properties probably similar to the official oil of savin.	....	....
Cedar-wood (American).	Wood of *J. Virginiana.*	2.5–5.0	0.940–0.900	—30 to —40	....	Cedrene; cedar-camphor, $C_{15}H_{26}O$.	Oil-immersion lenses.
Cedrat.	(See *Citron Oil.*)						
Cedrela Wood.	Wood of *Cedrela odorata.*	0.5	0.9348	—0.3	Light blue.	Probably cadinene.	....
Celery.	Fruit of *Apium graveolens.*	....	....	....	....	Dextro-limonene, but no pinene (distinction from oil of turpentine); a very small quantity of palmitic acid and phenols; sedanolide, $C_{12}H_{18}O_2$; sedanonic acid, $C_{12}H_{18}O_3$.	....
	S. & Co.	....	0.880–0.890	+ 67	....		
	B. & Co.	....	0.8730; 0.8777	+ 75; + 71.6	....		
	Green herb of *A. graveolens.*	....	0.848–0.850	+ 48 to + 52	....	....	....

Chamomile, German	Flower-heads of *Matricaria Chamomilla.*	0.1 tn 0.3	0.930–0.945	Very slight.	Bluish colour, changing to green and brown on exposure to light. *Bitter taste.*	Solidifies to a buttery mass at a low temperature, owing to the presence of a paraffin, melting at 53°–54° C. *The oil appears to contain esters.*	....
Roman.	Flower-heads of *Anthemis nobilis.*	0.5 to 1.0	0.905–0.915	Slight.	Bluish colour when fresh, changing in the light to greenish or brownish-yellow. Burning taste.	Isobutyl isobutyrate and angelate; amyl and hexyl tiglates and angelates; anthemol, $C_{10}H_{16}O$. The ester content appears to be much less than that of English oils (containing 80 per cent. esters).	
	Brit. Pharm.	....	0.905–0.915				
Champaca. (See *Guaiacum-wood oil.*)	Flowers of *Michelia Champaca.* Java.	....	0.914	—13.25	Odour somewhat resembling oil of orris.	Benzoic acid or a benzoate.	....
	Manila.	....	0.938	—54.1	Fragrant light *brown liquid.* Deposits abundant crystals at ordinary temperatures.		
	Flowers of *Michelia longifolia*, Java.	....	0.883	—12.8	Very volatile, odour resembling basilicum.		
Cheken-leaf.	Leaves of *Myrtus cheken.*	1.0	0.880	+ 20	Yellow-green colour, pleasant odour.	Pinene; cineol.	....
Chenopodium (American Wormseed).	*Fruit of Chenopodium ambrosioides.*	1.0					Anthelmintic.
	Commercial Oils.	....	About 0.970	—5 to —6.3	Penetrating odour and bitterish taste. Varies in character according to age.	Stated to contain a hydrocarbon ($C_{10}H_{16}$) and a body containing $C_{10}H_{16}O$.	
	S. & Co.	....	0.910	—19			
	Leaves of *C. ambrosioides.*	....	0.879	—33	Odour of trimethylamine.		
Chervil.	Seeds of *Chærophyllum sativum.*	0.01	....	....	Odour of anise and estragon oils.	Estragol; a paraffin.	....

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Chione Glabra.	Bark of *Chione glabra* (West Indies).	....	....	....	Curious and objectionable odour.	Ortho-hydroxy-acetophenone.	....
Cinnamon, Ceylon.	Bark of *Cinnamomum zeylanicum.*	0.5–1.5	1.025 to 1.035	0° to —1	Sol. in alcohol.	Cinnamic aldehyde; phellandrene; eugenol.	(See p. 44.)
Cinnamon, Japanese.	(*See Nikkei Oil.*)						
Cinnamon Leaf.	From *C. zeylanicum.*	1.5 to 2.0	1.045 to 1.065	—1 to + 1	....	Eugenol; cinnamic aldehyde; safrol.	(See p. 45.)
Citron.	Fresh peel of *Citrus medica.*	....	0.870	+ 66	....	Limonene; citral.	....
Citron (Cedrat), Expressed oil.	Fresh peel of *Citrus medica* (*Citrea Gibocarpa*).	....	0.851	+ 80	Refractive Index, 1.475 at 20°. Contains minute white crystals.	Citral, about 6 per cent.; limonene; dipentene (?); a crystalline substance containing $C_{18}H_{18}O_6$.	....
Citronella.	Grass of *Andropogon Nardus.*	....	0.890–0.910	To —14	....	Citronellal; geraniol; borneol; linalol; camphene; dipentene; limonene; methyl heptenone.	Perfumery; perfuming soaps, &c.
Citronella (Java Verbena).	Fruit of *Tetranthera citrata.*	5.0	0.895–0.980	....	Verbena-like odour, and has therefore been called "Oil of Verbena, Java."	Citral; a terpene.	....
Clove.	Flower-buds of *Eugenia caryophyllata.*	14–19	....	....	....	....	Medicine; flavouring, &c.
	Brit. Pharm.	....	Not below 1.050	....	....		
	S. & Co.	....	1.045–1.070	Slightly lævorotatory (to —1).	Boils between 250–260° C., greater part distilling between 250–251° C. Becomes darker and thicker with age. Spicy taste.	Methyl alcohol; furfurol; 80–90 per cent. of eugenol; caryophyllene; acetyl eugenol.	....
	Flower stems.	....	1.040–1.065	To —1.3	Odour not so fine as true oil of clove.	Methyl alcohol; furfurol; eugenol; caryophyllene.	....
Clove Root	Root of *Geum urbanum.*	....	....	....	Exceedingly agreeable cinnamon-like odour.		

Cochlearia (synthetic).	....	....	0.944 (at 12° C.)	....	Boiling-point 159–160° C. In commerce a mixture consisting of oil of mustard and oil of rue is frequently sold as oil of Cochlearia, but has not the properties of the true oil.	Secondary butyl thiocarbimide.	....
Cognac.	....	....	0.876–0.883	—0.05 to + 0.75	Acid-number 37 to 70; ester-number 140 to 219; sol. in 2 parts of 80 per cent. alcohol.	....	....
Conium.	Fruit of *Conium maculatum.*	0.02	0.831	—2.2	....	....	....
	Herb of *C. maculatum.*	0.08	0.931 at 20°	....	....	....	....
Copaiba.	Oleo-resin of *Copaifera Lansdorfii,* and other species.	....	0.890–0.910	Lævorotatory to —2	Bitterish and pungent taste. Has same effects upon the system as copaiba.	Chiefly caryophyllene.	Medicine.
	S. & Co.	....	0.900–0.910	—8.1	....	....	....
Coriander.	Fruit of *Coriandrum sativum.*	0.2–1.0					
	Brit. Pharm.	....	0.870–0.885	+ 5 to + 15	Warm, spicy taste.	Dextro-linalol (Coriandrol); pinene.	....
Costus.	Root of *Aplotaxis lappa.*	1.0	0.980–0.987	+ 15 to + 16	....	....	....
Cubebs.	Unripe fruit of *Piper Cubeba.*	10–18	About 0.920	....	Pale-greenish or yellowish oil, with a warm, camphoraceous, aromatic taste.	Chiefly cadinene, with some dipentene. When old, or distilled from old fruit, also contains cubeb camphor.	Medicine.
	S. & Co.	....	0.910–0.930	—30 to —40			
	B. & Co.	....	about 0.930	—30 to —25			
Culilaban.	Fruit of *Cinnamomum Culilavan.*	3–4	1.051	....	Odour of eugenol; dark in colour.	Eugenol; methyl-eugenol.	....

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Cumin.	Fruit of *Cuminum cyminum*.	2.5–4.0	0.890–0.930	+ 4 to + 6	Limpid liquid with a sharp spicy taste.	Cymol; cumin aldehyde, $C_{10}H_{12}O$.	....
Cypress.	Leaves of *Cypressus sempervirens*.	....	0.882–0.887	+ 4 to + 0	....	*d*-Pinene; *l*-cadinene; furfural; *d*-camphene; *d*-sylvestrene; cymene; a ketone; sabinol; acetate of *d*-terpineol (m.-pt. 35°); valeric acid; cypress camphor.	Medicine.
	S. & Co.		0.892	+ 16.5	Sol. 1 : 2.5 of 90 per cent. alcohol.		
Damiana.	*Turnera microphylla* and other species.	....	0.940–0.990	—23.9	Greenish viscid liquid, with an odour of chamomile. Boils between 250° and 310° C.	A blue oil in the higher fractions; a paraffin.	....
Dill.	Fruit of *Peucedanum graveolens*.	3–4	0.895–0.915	+ 70 to + 80	Penetrating odour, and sweetish, afterwards sharp and burning taste. Odour quite different from East Indian dill oil.	*Limonene*; *carvone*; a paraffin.	....
	Brit. Pharm.	....	0.905–0.920	+ 70			
East Indian.	*Anethum sowa*.	2–3	0.970	+ 41.5		Limonene; dill-apiol; carvone.	
Dog-fennel.	Entire plant of *Eupatorium fœniculaceum*.	....	0.935	+ 17.9	....	Phellandrene.	....
Elder Otto.	Elder blossom (*Sambucus nigra*).	....	0.8461 (at 30° C.)	....	Melting-pt., 28.2° C.; saponification-number 75.4; after acetylation, 97.7.	....	....
	B. & Co.	....	0.8277 (at 30° C.)	....	Melting-pt., 29° C.	....	....

Elemi.	Oleo-resin of *Manila Elemi of uncertain botanical origin.*	....	0.870–0.910	+ 45	*Agreeable aromatic odour and taste.*	Phellandrene; dipentene: *the higher fractions probably containing polyterpenes and oxygenated compounds.*	Perfumery.
Elecampane.	Root of *Inula helenium.*	1.0–2.0	....	....	....	Alantic acid $(C_6H_8O)x$; alanto-lactone; alantol.	....
Erigeron (or Fleabane).	Fresh flowering herb of *Erigeron Canadensis.*	0.5	0.855–0.890 (increasing with age).	+ 52	Peculiar persistent odour and slightly pungent taste. Larger part distils between 175° and 180° C.	Limonene; terpineol, and esters.	Medicine.
Eriodictyon.	Leaves of *E. Californica.*	0.1	0.937	— 1.6	Sol. in 70 per cent. alcohol.	(Unknown.)	....
Estragon (Tarragon).	Herb of *Artemisia Dracunculus.* *S. & Co.* Commercial Oils.	0.1 to 0.8	0.890–0.960 0.920–0.960	+ 2 to + 9 + 2.5 to + 9	Peculiar odour.	Methyl-chavicol.	....
Eucalyptus.	(See page 424.)						
Fennel.	Fruit of *Fœniculum capillaceum* and other species.	1.0–6.0	....	....	Between 5° and 10° usually solidifies to a crystalline mass.	Pinene; phellandrene; dipentene; limonene; cymene (?); fenchone; anethol (usually about 60 per cent.). Oils from different sources never contain all these constituents simultaneously.	Medicine.
	S. & Co. *B. & Co.* Commercial Oils.	....	0.965–0.975 0.908 0.960–0.980	+ 7 to + 22 + 27.6 + 6 to + 20	Boiling-point 100° to 220°.	Tardy found (in addition to some of the above) methyl-chavicol; anisaldehyde; anisic acetone; anisic acid; and an unknown substance, containing $C_{13}H_{14}O_2$.	
Feverfew	(See *Pyrethrum Oil.*)						
Fir-Cone.	(See page 455.)						

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.)	Other Characters.	Known Constituents.	Applications.
Fleabane.	(See *Oil of Erigeron.*)						
Fœnugreek.	Seeds of *Trigonella fœnumgræcum.*	0.014	0.870	+ 8	Light brown oil; sol. in 90 per cent. alcohol.	....	....
Frankincense.	(See *Oil of Olibanum.*)						
Galangal.	Rhizome of *Alpinia officinarum.*	0.5–1.5	0.915–0.925	—1 to —4	Boils between 170° and 275° C.; sol. in ½ parts of 90 per cent. alcohol.	Cineol; eugenol (25 per cent.).	....
Galbanum.	Gum-resin of *Ferula galbaniflua.*	14–22	0.910–0.940	—10 to + 20	Yellowish oil of aromatic odour.	*d*-pinene; cadinene.	....
Gardenia.	Fresh flowers.	0.07	1.009	+ 3.0	Boils at 204° C. with partial decomposition.	Benzyl acetate; styrolyl *acetate*; *linalol*; *linalyl* acetate; terpineol; methyl anthranilate; esters of benzoic acid.	....
Garlic.	(See page 386.)						
Geranium (Rose Geranium).	Herb of several species of *Pelargonium*, especially *P. Radula*, *P. capitatum* and *P. odoratissimum*.				Pale yellowish or greenish (Réunion) oil, having an agreeable rose-like odour.	Geraniol and citronellol (free, and combined as tiglates).	Perfumery.
	Algerian.	....	0.890–0.898	—7 to —9			
	French.	....	0.894–0.899	—9 to —12			
	Réunion.	....	0.886–0.895	—8 to —11			
	Spanish.	....	About 0.898	About —8			
	S. & Co.	....	0.906	—16			
	B. & Co.	....	0.885–0.905	—8 to —12	....	Total alcohols 60 to 75 per cent. (of which 15 to 25 per cent. exist as esters).	....

Geranium, East Indian (so-called **Turkish geranium** or **Palmarosa oil**).	From grass of a species of *Andropogon*, probably *A. Schœnanthus.*	0.3–0.4	....	....	....	Geraniol; geranyl acetate and capronate; dipentene; methyl heptenone (?).	....
	S. & Co.	....	0.888–0.896	—1.7 to + 1.8	....	Total alcohols 75 to 95 per cent. (of which less than 10 per cent. exist as esters), consisting chiefly of geraniol, with very little or no citronellol.	
	B. & Co.	....	0.885–0.895	Not more than + 1 or —1	....		
Ginger.	Rhizome of *Zingiber officinale.*	2.0–3.0	0.875–0.885	—26 to —44	Aromatic, somewhat burning taste.	Campene; phellandrene; *l*-zingiberene.	Preparation of liqueurs.
	B. & Co. African.	....	0.8870	—37.5			
		....	0.8820	—45.3			
	B. & Co. Cochin.	....	0.8869–0.8998	—12.4 to —27.4			
Golden Rod (Canadian).	Flowering herb of *Solidago Canadensis*, etc.	....	0.859	—11.2	....	Contains 85 per cent. of terpenes, mainly pinene with a little phellandrene and dipentene; possibly limonene; borneol; bornyl acetate; cadinene.	....
Grains of Paradise.	Seeds of *Amomum melegueta.*	0.75	0.894	—4	Distils mainly at 257°–258° C.	Body of formula, $C_{22}H_{32}O$.	....
Grape-fruit (Shaddock).	Fruit of *Citrus decumana.*	....	0.865; 0.860	+ 94.5	Odour of bitter orange oil.	....	....
Guaiacum Wood ("Balsam Wood").	Wood of guaiacum species, probably *Bulnesia sarmienti.*	....	0.968 at 30° C.	—6.5 at 30°C.	Very viscid oil. Violet and tea-like odour, and crystalline at ordinary temperatures.	Crystallisable guaiac-alcohol, $C_{14}H_{24}O$ or $C_{15}H_{26}O$, m.-pt. 91° C. ("Champacol"). A sample of so-called "Champaca-wood oil" was found by S. & Co. to be Guaiacum-wood oil.	Perfumery; perfuming soaps, &c.
Gurjun Balsam.	Balsam of *Dipterocarpus* species.	....	0.920–0.930	—35 to —106	Distils mainly at 255°–256° C.	A sesquiterpene; small amounts of alcohols.	....
Hedeoma, American.	Dried leaves and tops of *Hedeoma pulegioides.*				Limpid liquid with a mint-like odour and taste. Forms a clear solution with 2 volumes or more of alcohol (70 per cent.).	Hedeomol ($C_{10}H_{18}O$); pulegone.	Medicine.
	U. S. Pharm.	....	0.920–0.935 (at 25°)	+ 18 to + 22			
	S. & Co.	....	0.925–0.940	+ 18 to + 22			

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Hedeoma (Pennyroyal).	Leaves of *Mentha pulegium*.	....	0.930–0.960	+ 17 to + 23	....	Pulegone.	....
Hedychium.	Flowers of *Hedychium coronarium*.	0.03	0.860	—0.5	....	....	....
Helichrysum.	Flowering herb of *Helichrysum stoechas*.	....	0.873	....	Distils mainly between 155°–170° C.	Pinene.	....
Hemp.	*Dried herb of Cannabis sativa.*	*0.1*	*0.932*	*—10 to —12*	....	*Terpenes; sesquiterpenes.*	....
Indian.	Herb of *C. Indica*.	....	0.930	....	....	Cannibene, $C_{15}H_{24}$.	....
Heracleum.	Fruit of *Heracleum Spondylium*.	1.0–3.0	0.80–0.88	+ 0.25	Acid reaction. Boils at 80°–300° C.	Ethyl butyrate; hexyl and octyl acetates; octyl capronate.	....
Hop.	Flowers of *Humulus lupulus*.	0.3–1.0	0.855–0.882	to + 1	....	Humulene; geraniol; tetrahydro-cymene (?); terpenes.	....
Horsemint (see Monarda Oil).	Herb of *Monarda punctata*.	....	0.930–0.940	slightly +	Yellowish-red or brownish-red colour and a strong thyme-like odour.	Thymol; cymol.	Liniments.
Hyssop.	Herb of *Hyssopus Officinalis*.	....	0.925–0.940	—19 to —23	Boils at 170°–218° C. Odour of thujone.	Possibly thujone or thujyl alcohol.	....
Iva.	Dried flowering herb of *Achillea moschata*.	0.5	0.932 to 0.934	....	Light blue colour. Boils between 170° and 260° C.	Cineol; "ivaol," a mixture of oxygenated bodies of unknown constitution.	....
Jasmine.	Flwrs. of *Jasminum grandiflorum*.	traces	1.007–1.018	+ 2.5 to + 3.5	....	Benzyl acetate; linalyl acetate; benzyl alcohol; linalol; indole; methyl anthranilate; jasmone ($C_{11}H_{16}O$).	....

Juniper.	Fruit of *Juniperus communis.*	0.5–1.5	0.850–0.890	....	Becomes dark and thicker by exposure to air. Has a somewhat terbinthinate and bitter taste.	Chiefly pinene with some cadinene; juniper-camphor.	Medicine; preparation of gin.
	Brit. Pharm.	....	0.865–0.890				
	S. & Co.	....	0.865–0.885	inactive or to —18			
Kæmpferia.	Rhizome of *Kæmpferia rotunda.*	0.2	0.945	+ 13.1	Odour at first of camphor, then reminding of estragon oil.	Cineol. Odour suggests probable presence of methyl-chavicol.	....
Kiku.	Leaves of *Pyrethrum Indicum.*	....	0.880–0.890	....	....	....	....
Kobushi.	Fresh leaves and twigs of *Magnolia Kobus.*	0.45	0.9642	—1.1	Sassafras-like odour.	Safrol; probably also citral.	....
Kuro-moji (Japan).	Wood of *Lindera sericea.*	....	0.890–0.915	—0.1	Balsamic odour.	Dextro-limonene; dipentene; terpineol; lævo-carvone.	Perfumery; perfuming soaps.
Lantana.	Herb of *Lantana camara.*	....	0.952	—0.25	....	....	....
Laurel.	Leaves of *Laurus nobilis.*	1 to 3	0.920–0.930	—15 to —18	....	Pinene; cineol; geraniol; eugenol; fatty acids.	....
Californian.	Leaves of *Umbellularia Californica.*	2.5 to 4.0	0.948	—22	Agreeable but afterwards irritating odour. Sol. in 1.5 parts 70 per cent. alcohol.	Umbellulone, $C_{10}H_{14}O$; cineol; eugenol; methyl-eugenol; *l*-pinene; safrol; fatty acids (traces).	....
Lavender.	Fresh flowers of *Lavandula officinalis. U. S. Pharm.*	....	0.885–0.897	....	....		
	French flowers. *S. & Co.*	....	0.883–0.895	—3 to —9	....	Linalol; linalyl acetate (30 to 45 per cent.); geraniol (?); sesquiterpene (?); small amounts of pinene and cineol.	....
	English Flowers. *S. & Co.*	....	0.885–0.900	—7 to —10	The content of esters in the French Oil is usually about three times as high as English Oil.	Much cineol; limonene; linalyl acetate (7 to 10 per cent.); a sesquiterpene. Chiefly linalyl acetate (10.7 per cent. esters).	....
	English Flowers. *B. & Co.*	....	0.8838	—9.8			

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Lavender.	Spanish Flowers.		0.916; 0.912	+ 16.4; +13.3	....	These oils contained 3.15 per cent. and 3.4 per cent. of esters (as linalyl acetate), and 44.5 and 50.5 per cent. free alcohol (as linalol). They probably contained some Lavender Spike oil.	
Portuguese.	Flowers of *L. pedunculata.*	....	0.939	—44.9	Indistinct and not very pleasant odour.	Linalyl acetate 39 per cent.; thujone; cineol.	....
	Flowers of *L. dentata.*	....	0.926	....	Distils almost completely between 170–200° C. Has an odour resembling rosemary and camphor.	Cineol.	....
	Flowers of *Lavandula Stœchas.*	....	0.942	....	Distils between 180–245° C. Has an odour resembling rosemary and camphor.	Cineol.	....
Lavender, Spike.	Flowering herb of *Lavandula spica.*	....	0.905–0.915	+ 1 to + 4, rarely to + 7	Much less fragrant than the official oil. Has odour reminding both of rosemary and lavender.	Pinene; camphene; cineol; linalol; camphor; borneol; terpineol (?); geraniol; practically no esters.	Veterinary medicine.
Ledum.	(See *Marsh-Tea Oil.*)						
Lemon.	Fresh lemon-peel of *Citrus medica,* var. *limonum.*	....	0.858–0.861	+ 59 to + 67	Bitterish taste.	Limonene; citral; citronellal; and according to Umney and Swinton, geranyl acetate; possibly also other esters of geraniol and citronellol.	Perfumery; flavouring agent.
	Brit. Pharm.	....	0.857–0.860	+ 59 (not less)	....	....	....

Lemongrass (Verbena; Indian Melissa).	Grass of *Andropogon citratus.*	....	0.895–0.905	+ 1 to —3	Fragrant odour, reminding of lemon and verbena	Citral; geraniol; methyl-heptenone.	Perfumery.
	B. & Co.	....	0.9023	—12.7	....	Aldehydes, 28 per cent.; alcohols (as $C_{10}H_{18}O$), 30 per cent.	
Lemon thyme.	....	....	0.898	—3	Distils chiefly between 210°–230° C.	Citral; thymol.	....
Lime, Italian.	Rind of fresh fruit of *Citrus limetta* (by expression).	....	0.882 0.872	+ 35 to + 40 + 58.25	Golden yellow oil, with refreshing odour.	Limonene; citral; linalol; linalyl acetate (26 per cent.).	Perfumery.
	Distilled oils.	....	0.8629–0.8656	+ 34.8 to +45	....	Citral (6.3 to 8 per cent.); and "limene," $C_{15}H_{24}$.	
Lime-flowers.	Flowers of *Citrus limetta.*	....	0.870	+ 21.5	....	Linalol; methyl anthranilate.	....
Lime, West Indian (Limette).	Rind of fresh fruit of *Citrus medica,* var. *acida* (by expression).	....	0.901 0.880–0.885	+ 36.3 + 35 to + 40	Lemon odour. 18 per cent. of non-volatile residue.	A paraffin; citral; limonene; methyl anthranilate.	....
	Distilled oil.	....	0.866	+46.6	Unpleasant odour. 3 per cent. non-vol. residue.	....	....
Linaloe (Lignaloe).	Mexican wood of *Bursera* species.	7.0–12.0	0.880	—13 to +8	....	Chiefly linalol, with terpineol, methyl-heptenone, and small amount of geraniol.	Perfumery.
	S. & Co. Guiana wood (*Bois de rose femelle*).	.... 1.0–1.6	0.875–0.895 0.875	—5 to —12 —16.0	Fragrant oil. Resembles the Mexican wood oil.	.... Linalol (almost wholly).	.... Perfuming soaps.
Lovage.	Dried root of *Levisticum officinale.*	0.6–1	1.00–1.045	0 to + 7	Sol. in 2 to 3 parts of 80 per cent. alcohol.	*d*-terpineol; a terpene.	....
	B. & Co.	....	0.963–1.023	—14 to + 12	....	....	....
Mace.	Arillode of seed of *Myristica fragrans.*	4.0–15.0	0.910–0.930	+ 10	Agreeable odour.	Pinene; dipentene; myristicin.	....
Mandarin.	(See *Orange Oil, Mandarin.*)						
Marjoram.	Fresh herb of *Origanum Marjorana.*	0.3–1.0	0.902–0.904	+ 20	....	Terpenes (including terpinene, 40 per cent.; terpineol, 60 per cent.; traces of acetates and a sesquiterpene).	....

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Marsh Tea (Ledum).	Herb of *Ledum palustre.*	0.5–1.0	....	....	Pale reddish-yellow colour and penetrating odour. Boils between 180°–250° C.	Chief constituent said to be Ledum-camphor, $C_{15}H_{26}O$.	....
	Leaves.	....	0.932				
	Flowering twigs.	....	0.963	....		....	....
Masterwort.	Root of *Imperatoria ostruthium.*	1.0	0.875	....	....	Angelic aldehyde (?).	....
Massoy Bark.	Bark of *Massoia aromatica.*	6.0–8.0	1.04–1.06	....	Agreeable spicy odour reminding of clove and nutmeg, and a sharp burning taste.	Eugenol (75 per cent.); safrol; pinene; limonene; dipentene.	Perfuming soaps, &c.
Mate.	Dried leaves of *Ilex Paraguayensis.*	0.77	.8875	+ 3.73 at 20°	Solid, melts at 26.5° C. Sol. in absolute alcohol.	....	....
Matico.	Leaves (and flowers) of *Piper angustifolium.*	0.5–3.5	....	....	Yellowish - brown colour and peculiar odour.	Dill-apiol; small amount of parsley-apiol; a phenol, possibly methyl-eugenol; a substance solidifying at —18°.	....
	Leaves.	....	0.93–1.07	+ 5.6			
	Flowers.	....	1.132	....			
Meadowsweet.	Herb of *Spiræa ulmaria.*	....	....	....	....	Salicyl-aldehyde; a terpene.	....
Melaleuca.	Leaves of *Melaleuca acuminata*	....	0.892	—15.3	....	Cineol; terpineol.	....
	Leaves of *M. leucadendron*	....	0.955	—3.7	....	....	....
	Leaves of *M. uncinata*	....	0.925	+ 1.7			
Melissa.	Herb of *Melissa officinalis.*	traces	0.895–0.925	—0.5 to —6.5	....	Citral; citronellal; geraniol; linalol; citronellol.	....
Mew.	Dried root of *Meum athamanticum.*	0.7	1.001	....	Above 300° C. gives greenish-blue fractions.	....	....

Michelia.	(See *Champaca Oil.*)						
Monarda (see Horsemint Oil).	Herb of *Monarda punctata* (Horsemint).	3.0	0.930–0.940	slightly +	Thymol separates on standing.	Thymol 60 per cent.; cymene; traces d-limonene; linalol (?); carvacrol (?).	....
	M. fistulosa (wild bergamot).	....	0.916–0.941	slightly —	....	Carvacrol 55 per cent.; thymoquinone; thymohydroquinone; cymene; limonene.	....
	M. citriodora.	1.0	0.944 (at 20° C.)	....	....	Carvacrol; thymo-hydroquinone; citral 1 per cent.; cymene (?).	....
Mountain mint.	Herb of *Pycnanthemum incanum.*	1.0	0.910 to 0.940	+ 3 to + 5	....	Carvacrol; pulegone.	....
Mugwort.	(See *Artemisia oil.*)						
Muskroot.	Rhizome of *Ferula sumbul.*	0.2 to 0.4	0.954 to 0.964	....	Sol. in equal vol. of 90 per cent. alcohol.	....	....
Mustard.	(See Vol. III, Pt. 3.)						
Myrcia.	(See *Bay Oil.*)						
Myrtle.	Leaves of *Myrtus communis.*	0.3	0.890 to 0.920	+ 10 to + 30	....	Pinene; cineol; dipentene; linalol (?).	....
Neroli.	(See *Orange-flower Oil.*)						
Nigella.	Seeds of *Nigella sativa.*	0.46	0.875	+ 1.5	Boils between 170° and 260° C.	....	....
	Seeds of *Nigella damascena.*	0.5	0.906	+ 1	Blue fluorescence.	Damascenine, $C_{10}H_{15}NO_3$.	....
Nikkei.	Leaves and young twigs of *Cinnamomum loureirii.*	0.2	0.9005	—8.75	Yellow oil of pleasant odour, recalling citral and cinnamon.	Aldehydes, 27 per cent., chiefly citral; linalol (40 per cent.); cineol.	....
	Root Bark.	....	0.982	....	....	Cinnamic aldehyde.	....
Nutmeg.	Fruit of *Myristica fragrans.*	8.0–15.0	....	....	Darkens and thickens on exposure to air. *Spicy taste.*	Chiefly pinene and myristicin.	....
	Brit. Pharm.	....	0.870–0.910	....	....	....	....
	S. & Co.	....	0.865–0.920	+ 14 to + 30	....	....	....

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Olibanum.	Gum-resin of *Boswellia Carterii* and other species.	4.7	0.875–0.885	—11.5	Balsamic odour.	Chiefly lævo-pinene; some phellandrene; dipentene; cadinene; and oxygenated bodies.	Perfuming soaps, &c.
Onion Oil.	Fresh herb and bulb of *Allium cepa*.	0.05	1.037	—5	Dark brown oil.	Allyl propyl disulphide. Allyl sulphide and terpenes are absent.	....
Orange Flower (Neroli Oil).	Fresh flowers of *Citrus bigaradia* (Bitter Orange).	....	....	....	Fragrant odour and somewhat bitter taste.	Limonene (20 per cent.); linalol (30 per cent.); linalyl acetate (40 per cent.); geraniol (30 per cent.); nerol; a paraffin.	Perfumery.
	S. & Co.	....	0.870–0.885	to + 10	....	....	....
	Fresh flowers of *Citrus aurantium* (Sweet Orange).	....	0.870–0.890	+ 16 to + 29	....	....	....
Orange Peel (by expression).	Fresh peel of *Citrus bigaradia* (Bitter Orange).	....	0.853 to 0.854	+ 91 to + 98	....	Chiefly limonene. The oil from the sweet orange also contains citral, with minute portions of oxygenated substances (citronellal and another aldehyde).	Perfumery, flavouring agent.
	Citrus aurantium (Sweet Orange).	....	0.848 to 0.852	+ 96 to + 99	....	....	....
	Expressed from *unripe fruit.*	....	*0.853*	+ 76.8	....	....	....
Orange, Mandarin.	Expressed from fresh peel of *Citrus madurensis*.	....	0.850–0.860	About + 70	....	Limonene; citral; probably citronellal; methyl ester of methyl anthranilate.	....
Orange, Tangerine.	....	....	0.855	+ 69	....	Limettin (?).	....

Origanum.	Herb of *Origanum hirtum.*	2 to 3	0.940–0.980	Inactive or slightly —	Golden yellow colour when freshly rectified, reddish or reddish-brown on keeping. Penetrating, aromatic, thyme-like odour.	Carvacrol (60 to 85 per cent.). Should not contain less than 50 per cent.	Microscopy, etc.
	Herb of *Origanum smyrnæum.*	....	0.915–0.945	—3 to —13	....	Cymol; linalol; carvacrol (30–60 per cent.).	....
Orris root.	Rhizomes of several species of *Iris* (*I. germanica* and *I. pallida*, &c.).	0.1 to 0.2	....	Slightly +	Melts at about 40° to 50° C. Exquisite and persistent odour.	Myristic acid (about 90 per cent.); oleic acid; methyl oleate and myristate; oleic aldehyde; irone, 10 to 15 per cent.	Perfumery, such as floral extracts, soaps, etc.
Orris Otto.		....	0.9489	—20.5	Soluble in 70 per cent. alcohol, 1 : 8. Congeals at —5° C.	....	....
Palmarosa.	(See *Geranium Oils.*)						
Paracoto.	Bark of a species of *Monimiaceæ* or *Lauraceæ.*	....	0.927–1.018	—2 to + 6	Colourless oil of pleasant odour.	Cadinene; methyl-eugenol.	....
Parsley.	Fruit of *Petroselinum sativum. S. & Co.*	2.0 to 6.0	1.05–1.10	—7.3	*Colourless or pale* greenish-yellow.	*Pinene; apiol.*	*Diuretic.*
	Root of *P. sativum.*	....	1.00 to 1.05	—2 to + 1.5	Deposits crystals, probably apiol.	....	....
Pastinac.	Fruit of *Pastinaca sativa.*	1.5 to 2.5	0.870–0.890	—0.2 to —0.5	A yellow oil.	Ethyl alcohol; octyl butyrate; octyl propionate.	....
Patchouli.	Leaves of *Pogostemon patchouli. S. & Co.*	2.0 to 4.0	.... 0.975–0.995	.... —50 to —65	Yellowish-green or brown, somewhat thick oil, with a *penetrating and* persistent odour.	Cadinene(?); cedrene; patchouli camphor; a liquid sesquiterpene-alcohol; *benzaldehyde; eugenol;* cinnamic aldehyde; a ketone.	....
	Leaves of a species of *Pogostemon* (from Java).	....	0.961	—32.2	Occasionally deposits a stearoptene.	A substance having an odour resembling anise aldehyde.	....
Pennyroyal.	(See *Oil of Hedeoma.*)						

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Pepper.	Fruit of *Piper nigrum*.	1.0–2.5					
	S. & Co.	....	0.880–0.905	—5	Strong pungent odour and taste.	Phellandrene; dipentene.	....
	B. & Co.	....	0.930	—8.5	....	....	....
	Fruit of *Piper longum* (Long pepper). *S. & Co.*	....	0.861	....	Thickish oil of a light green colour, odour reminding of ginger. Boils at 250°–300° C.	....	....
Pepper, Japanese.	Fruit of *Xanthoxylum piperitum*.	....	0.973	....	....	Citral.	....
Peppermint Oils.	(See page 449.)						
Persea.	Dried leaves of *Persea gratissima*.	0.5	0.960	+ 1.9	Greenish oil; refractive index at 18° C., 1.5164.	Methyl-chavicol; pinene; a paraffin.	....
Petit-grain.	Leaves, twigs and unripe fruits of *Citrus bigaradia*.	....	....	....	*Odour resembling* neroli oil.	Limonene; *linalol*; *nerol*; linalyl acetate; a sesquiterpene.	*Perfumery.*
	S. & Co.	....	0.887–0.900	—1.3 to + 3.7	....	....	....
	B. & Co.	....	0.8907; 0.8908	—1.1; —3.8	....	....	....
Petit-grain citronnier.	Leaves and twigs of *Citrus medica*.						
	S. & Co.	....	0.869 to 0.874	+ 22 to + 34	Contains oil from unripe fruit.	Esters (as linalol), 4 per cent.; citral.	....
	B. & Co.	....	0.878	+ 9.4	....	Esters (as linalol), 10 per cent.; citral, 11 per cent.	....
Peucedanum.	Root of *Peucedanum grande*.	traces	0.900	+ 30 to + 35	Boils at 185–228° C. leaving large residue.	....	....

Pichurim bean.	Seeds of *Nectandra pichury.*	0.5 to 1.0	....	....	Fraction distilling between 255° and 256° C. is of a deep blue colour.	Pinene; esters of lauric and valeric acids (?); safrol (?).	....
Pimento (Allspice Oil).	Nearly ripe fruit of *Pimenta officinalis.*	3.0–4.5	1.045–1.055	....	Becomes darker and thicker by age and exposure to the air. Clove-like odour and pungent spicy taste.	Eugenol; a sesquiterpene. Closely resembles clove oil in composition and properties.	Aromatic stimulant.
Pimpinella.	Dried root of *Pimpinella saxifraga.*	....	0.960	....	Unpleasant odour resembling parsley. Boils at 240°C.	....	....
Pine-needles.	(See page 455.)						
Pittosporum ("Mock-orange")	Fruit of *Pimpinella undulatum.*	0.4	0.861	+ 74	....	Limonene, 75 per cent.; a sesquiterpene; traces of esters.	....
Poplar.	Young buds of *Populus nigra.*	0.3–0.6	.900–.905	+ 2 to + 6	Odour of chamomile. Boils at 260° C.	Humulene and another sesquiterpene; a paraffin.	....
Pyrethrum (Feverfew).	Flowering or dried herb of *Pyrethrum parthenium.*	0.1–0.4	0.900–0.960	....	Sap. value, 131.	Borneol and bornyl esters; camphor (?).	....
Ragweed.	Flowering herb of *Ambrosia artemisifolia.*	0.1	0.870	—26	Deep green colour.	....	....
Rhodium.	(See *Rosewood Oil.*)						
Rose.	Fresh flowers of *Rosa damascena.*	0.02	....	....	Fragrant odour, and mild, sweetish taste. Congealing-pt. about 16° to 21° C.	Geraniol; citronellol; a paraffin.	Perfumery; flavouring.
	Brit. Pharm.	....	0.856–0.860 (at 30° C.)	....	....		
	U. S. Pharm.	....	0.855–0.865 (at 25° C.)	....	Congeals at 18–22° C.	Sap. value, 10–17.	....
	S. & Co.:— Bulgarian Oil.	....	0.855–0.870 (at 20° C.)	0 to —4	....	....	....
	German Oil.	....	0.845–0.855 (at 30° C.)	+ 1 to —1	....	....	....

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Rosemary.	Flowering tops of *Rosmarinus officinalis.*	1.4	.900 to .918	+ 1 to + 12	....	Pinene; camphene; cineol; camphor; borneol and bornyl acetate.	....
	Brit. Pharm.	....	.900–.915	to + 10	....		
Rosewood (Rhodium).	Wood of *Convolvulus scoparius* and *C. floridus.*	....	0.900 to 0.910	....	Thick yellow oil of rose-like odour, crystallising in needles at about 12° C. Commercial oil invariably mixture of rose and geranium oils, &c.	Apparently chiefly a sesquiterpene.	Perfumery.
Rue.	Herb of *Ruta graveolens. S. & Co.*	0.06	.833–.840	+ 0.2 to + 2.1	Greenish-yellow colour and characteristic odour. Solidifies at 8 to 10° C. Boils at about 215–235° C.	About 90 per cent. of methyl-nonyl-ketone; lauric aldehyde; small amounts of methyl-heptyl-ketone; methyl ester of methyl anthranilic acid.	Medicine.
Algerian.	....	....	0.842	+ 5	Blue oil in high fractions (0.5 per cent.). Ketone solidifies at —16° C. Both rue oils sol. in 2–3 vols. of alcohol (70 per cent.).	Methyl-heptyl-ketone; small amount of methyl-nonyl-ketone; an acetic ester; methyl-heptyl and methyl-nonyl carbinols; pinene; *l*-limonene; cineol, &c.	....
Saffron.	Stigmas of *Crocus sativus.*	....	....	....	....	Pinene; cineol; a paraffin; an oxygenated body; palmitic and stearic acids.	....
Sage.	Leaves of *Salvia officinalis.*	1.0–3.0	.915–.930	+ 12 to + 25	Penetrating characteristic odour.	Thujone; borneol; pinene; cineol.	Medicine.
Sage (Clary).	Leaves of *Salvia sclarea. S. & Co.*	....	0.907–0.928	—24	Odour of linalyl acetate.	Linalyl acetate (?).	....
Sandal-Wood.	Wood of *Santalum album.*	1.5–6.0	....	....	Yellow thickish oil, peculiar odour and pungent spicy taste.	Santal alcohols (94 to 98 per cent.); santalol, 3 per cent.; *a* & *b*-santalenes; santalic acid; teresantalic acid; esters of santal alcohols.	Perfumery and medicine.

Sandal-wood. (East Indian).	*Brit. Pharm.*	....	0.975–0.980	—1.6 to —20		....	....
	S. & Co.	....	0.970–0.980	—17 to —19	Saponification figure of the pure oil does not exceed 15.	....	....
	B. & Co.	....	0.971–0.982	—10.8 to —17.7	....	....	....
(West Indian.)	Unknown. *S. & Co.*	....	0.963–0.967	+ 24 to + 29	....	....	....
(African.)	Unknown (from Madagascar). *S. & Co.*	....	0.969	....	Ruby-red colour.	....	....
(W. Australian.)	*S. cygnorum.*	....	0.953	+ 5.3	Sharp resinous empyreumatic odour.	Contains less santal alcohols than East Indian Oils.	....
(S. Australian.)	*S. Preissianum.*	....	1 022	....	Cherry-red colour. Solidifies at about 6° C.	A crystalline alcohol boiling at 101°–103° C.	....
Sassafras.	Leaves of *Sassafras officinalis.*	3.0–8.0	0.872	—6.5	....	Linalol; pinene; phellandrene; cadinene; a paraffin melting at 57° C.	....
	Root-bark of *S. officinalis.*	....	1.065–1.095	+ 1 to + 4	Reddish-yellow oil with a warm taste.	Safrol, 80 per cent.; camphor; pinene; phellandrene; eugenol; cadinene (?).	....
Satureja.	Herb of *Satureja Thymbra. S. & Co.*	....	0.906	....	Strong and penetrating thymol-like odour.	Cymol; thymol, 19 per cent; pinene; dipentene; bornyl acetate.	Stimulant; antiseptic.
	Fresh herb of *S. hortensis. S. & Co.*	....	0.898 to 0.924	+ 0.1	....	Carvacrol (30 per cent.); cymene (?); pinene (?); traces of another phenol.	....
	Herb of *S. montana* (Mountain Savory).	....	0.939	+ 2.5	Odour resembling common Savory oil.	Carvacrol; and according to Haller, another phenol and a terpene.	....
Savin.	Twigs of *Juniperus sabina.*	....	0.910–0.940	....	....	....	....
	U. S. Pharm.	....	0.903–0.923 (at 25° C.)	+ 40 to +60 (at 25°)	Becomes darker and thicker by age and exposure to air. Terebinthinate odour and pungent camphoraceous taste. Boils at 208° C.	Pinene; cadinene; sabinol ($C_{10}H_{16}O$), partly as acetate; cumin aldehyde (?).	Medicine.

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Savory.	(See *Satureja Oils.*)						
Serpentaria.	Rhizome and roots of *Aristolochia Serpentaria.* ("Virginian Snakeroot.")	1–2	0.975–0.988	—4	Amber colour, and an *odour resembling* valerian and camphor.	Pinene; an ester of borneol; *a body containing* $C_{18}H_{29}O$; and a bluish-green fraction.	....
Shaddock.	(See *Grape-fruit Oil.*)						
Snake-root.	(See *Asarum Canadense, A. Europæum*, and *Serpentaria Oils.*)						
Spearmint.	Fresh herb of *Mentha viridis.* *S. & Co.*	0.3–0.5	.... 0.920–0.940	.... to —43	.... Becomes darker and thicker by age and exposure to air. Strong characteristic odour and warm taste.	.... Carvone; pinene; limonene; linalol.	.... Medicine; soap perfumery.
Spike.	(See *Lavender Spike Oil.*)						
Spicewood.	Bark and twigs of *Laurus benzoin.*	0.4	0.923	....	Distils between 170°–300° C.	Terpenes; methyl salicylate (10 per cent.).	....
Spoonwort.	Fresh flowering plant of *Cochlearia officinalis.*	0.23	0.954	+ 55.5	*Distils between* 150°–162° C., leaving 5 per cent. of residue.	Secondary butyl thiocarbimide.	....
Star Anise.	(See *Anise Oil, Star.*)						
Sweet Birch.	Bark of *Betula lenta.*	....	1.175 *to* 1.187	Inactive.	*Boils at* 218–221°.	Methyl salicylate, 99.8%; an ester, and a paraffin, &c.	(See p. 89.)

Tansy.	Herb of *Tanacetum vulgare*.	0.1–0.2	....	....	Becomes brown on exposure to light and air. Poisonous.	Thujone ("tanacetone"); camphor; borneol.	Preparation of thujone.
	English Oil.	....	....	—27.5	....	....	....
	S. & Co. Fresh Herb.	....	0.915–0.930	+ 30 to + 45	....	....	....
	S. & Co. Dried Herb.	....	0.954	+ 30 to + 45			
Tansy Balsam.	Herb of *Tanacetum balsamita. S. & Co.*	0.06	0.943 to 0.949	—43.7 to —53.9	Balsamic odour, resembling common tansy. Distils between 207°–283°C.	Contains a paraffin.	
Tarragon.	(See *Estragon Oil.*)						
Tetranthera.	(See *Citronella Fruit Oil.*)						
Thuja.	Leaves of *Thuja occidentalis* (so-called White Cedar).	0.5–1.0	....	....	....	Thujone; *b*-fenchone; pinene; inactive carvone.	....
	Commercial Oils.	....	0.915–0.925	—8 to —14	....	....	....
	S. & Co.	....	0.922	—6.1	....	....	....
	Root of *T. orientalis.*	....	0.979	....	Intense brown colour.	....	....
Thyme.	Leaves and flowering tops of *Thymus vulgaris.*	0.3–2.5	0.900–0.930	Slightly —	Yellowish-red oil, pungent, afterwards cooling, taste.	Thymol, 20-30%; carvacrol; cymene; linalol; bornyl acetate; pinene ("thymene").	External stimulant in liniments, &c.
Thyme, Wild.	Dried herb of *Thymus Serphyllum. S. & Co.*	....	0.905–0.930	—1 to —11	Agreeable melissa-like aroma, with a slight odour of thyme.	Thymol; carvacrol; cymene.	....
	Herb of *T. camphoratus.*	....	0.904	....	....	Carvacrol (?).	....
	Herb of *T. capitatus.*	....	0.901	....	Strong thyme-like odour reminding somewhat of origanum.	Pinene; cymene; dipentene; bornyl acetate; thymol; carvacrol (?).	....
Tuberose.	Flowers.	....	....	....	Odourous fraction distils at 80°–180° C. at 15 mm. pressure.	A compound containing $C_{18}H_{20}O$.	Perfumery.
Turmeric.	Root of *Curcuma longa.*	5.0	0.940	....	....	Phellandrene.	....

Oil.	Chief Sources.	Yield (Per cent.).	Specific Gravity at 15° C.	Optical Rotation ° (100 mm.).	Other Characters.	Known Constituents.	Applications.
Valerian.	Root of *Valeriana officinalis.*	1.0	0.930–0.955	—8 to —15	Yellowish or brownish colour, characteristic, penetrating odour. Boils *between* 250–300° C.	Pinene; camphene; limonene (?); borneol; bornyl *formate, acetate, and iso*-valerate; terpineol (?); a sesquiterpene; an alcohol ($C_{10}H_{20}O_2$).	Medicine.
	Root of *Valeriana Celtica.*	....	0.967				
Japanese (Kesso Oil).	Root of *V. officinalis,* var. *angustifolia.*	*6 to 7*	0.990–0.996	—8 to —15	Green colour.	Similar to European root oil but containing also kessyl acetate, and a blue fraction.	Soap perfumery, &c.
Mexican.	Root of *Valeriana Mexicana.*	....	0.949	Inactive.	....	Valeric acid (about 89 per cent.).	
Verbena, East Indian.	(See *Lemongrass Oil.*)						
Java.	(See *Citronella-fruit Oil.*)						
Veti-vert.	Grass, *Andropogon muricatus.*	about 1.0	....	....	....	....	....
	S. & Co.	....	1.019–1.027	+ 25 to + 28	Most viscid of all essential oils.	....	....
	Réunion oil.	....	0.9995	+ 29; + 36	....	....	....
Wartara.	Seeds of *Xanthoxylum species.*	2.0	0.8714	+ 6.5	Coriander odour.	Linalol; dipentene; methyl cinnamate.	....
Wax-myrtle.	Leaves of *Myrica cerifera.*	....	0.886	—5.1	....	....	....
Wintergreen.	Leaves of *Gaultheria procumbens.*	0.5 to 1.0	1.175–1.187	—0.45 to —1	Boils at 218–221°.	Methyl salicylate, 99 per cent.; an aldehyde, &c.	(See page 88.)

Wormseed. American.	Flower-buds of *Artemisia maritima*, var. *Stechmanniana*. (See *Chenopodium Oil*.)	2.0	0.930–0.935	....	Marked poisonous properties.	Cineol; dipentene.	Limited use in medicine.
Wormwood.	Green herb of *Artemisia absinthium*.	0.2–0.9	.925–.955	....	Dark green colour when distilled from green herb. Unpleasant odour. *Markedly* poisonous.	Thujone (free and as acetate); thujyl alcohol; phellandrene; palmitic acid; acetic and iso-valeric acids (*as thujyl esters*); a blue fraction.	Limited use in medicine.
Ylang-Ylang (Cananga Oil).	Flowers of *Cananga odorata*.	....	....	....	Delicious odour.	Pinene; linalol; geraniol; iso-eugenol; linalyl and geranyl acetates and benzoates; cadinene; a crystalline alcohol; and para-cresol methyl-ether.	Perfumery.
	East Indian.	....	0.930–0.950	—40 to —45	....	....	....
	Java.	....	0.910–0.940	—20 to —55	....	....	....
Zedoary.	Root of *Curcuma Zedoaria*.	1.0–2.0	.99–1.01	....	Viscid dark coloured oil. Distils at 240°-300°.	Cineol; a crystalline body melting at 142.5°.	....

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